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CONTROL OF HAZARDOUS CHEMICAL SPILLS BY PHYSICAL BARRIERS

J. V. Friel, et al

MSA Research Corporation

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Control of Hazardous Chemical Spills by Physical Barriers

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CONTROL OF HAZARDOUS CHEMICAL SPILLS BY PHYSICAL BARRIERS

by

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ABSTRACT

The magnitude of potentially hazardous chemicals now being transported through the country poses a serious threat to the water ecosystem. Unless spills can be controlled at their source, movement into the water system may be inevitable. Such control dictates the availability of systems capable of forming dikes or flow diverting barriers either as a portable system carried on the vehicle or a mobile unit rapidly deployable to the site. In this regard, a program was instituted to investigate the applicability of foamed materials for forming such dikes and barriers. It was successfully demonstrated that polyurethane could be packaged in a portable unit and dispensed as a low density rigid foam capable of diking liquids on a variety of substrates (for example, dry concrete, asphalt, bare ground, vegetation). Attempts to develop a rigid high expansion system were not fully successful. A foamed concrete system was also successfully evolved, which used mobile equipment to build free form dikes. Modified surfactant foam was also shown to be an effective cover over spilled chemicals to control vapor release and fire hazards. In each case, a field tested unit was demonstrated or shown to be feasible.

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SECTION I

CONCLUSIONS

The conclusions to be drawn from the work conducted during this program primarily relate to the feasibility of the systems evolved. In three of the four phases, the basic objectives of the program were realized.

In the first phase, that concerned with polyurethane, it was demonstrated that a rigidized foam could effectively block or divert spills of a number of chemicals if applied under the correct conditions. These are water based liquids except strong acids, nonpolar organics, chlorine, and ammonia. Acids and polar organics are a question. The present formulation is not effective against methyl alcohol but is against acetone. The material is most effective on dry hard surfaces, but provides limited control on dirt, gravel, or vegetated ground. Adhesion to wet surfaces is poor and the diking of flowing streams is not possible. Some improvement with adhesion to wet surfaces was realized late in the program.

The urethane foam system can be packaged in a man-portable unit to yield an average of 5 cfm. Foam can be generated at densities as low as 0.3 lbs/ft^3 but 0.6 to 0.7 lbs/ft^3 is the optimum compromise between strength, adhesion, and foam yield. In this range, 60 to 70 cubic feet of foam are realized from the portable unit.

In the second phase, inorganic foam systems using concrete and a silicate gelling mechanism were evolved which allow the construction of barriers up to 2 ft in height without forms or supports. The height is limited by the ability of the gel set to support its own weight. Greater heights can be achieved with the development of some concrete set which has much greater strength but requires some 10 minutes cure time for its development. The material can be generated with commercially available continuous mixing equipment which is compact enough to be truck mobile. Final concrete density can be as low as 30 lbs/ft^3. The set material appears inert to most chemicals and attacked only slowly by the rest. With the correct procedure it can block flowing streams.

In Phase 4, soft detergent foam systems were shown to be capable of providing an insulating cover to hazardous spills reducing the ignition potential and toxic vapor release. Imine modified medium expansion foam 100 to 200:1 served adequately for most of the chemicals investigated. These imine foams were not successful with polar compounds. To control polar compounds, a low expansion system 50:1 incorporating a gellant was necessary. Of the available gelling materials, pectin provided the best results.

In Phase 3, attempts to evolve a high expansion (150:1 or greater) foamed material for diking were unsuccessful. Gelling of polymer foams such as polyvinyl alcohol (PVA) did not provide a sufficiently rigid material to be useful. Isocyanate-water foams rigidized but were permeable and lacked integrity. At higher density they approximated urethanes but were inferior in strength, adhesion, and impermeability.

SECTION II

RECOMMENDATIONS

The initial program has defined the potential of three systems: polyurethane, foamed concrete, and foam covers. For each of these materials sufficient data has been generated to allow delineation of a commercial package. Before such systems can be put into general use, however, further developmental work,to optimize the units and define their capabilities and limitations, appears warranted.

With the polyurethanes, significant changes in formulation have been made to adapt this material to the diking application. In this regard some problems have been experienced with shelf life of the packaged systems. Changes in material combinations would appear to be able to correct this deficiency. The allowable shelf life must also be determined.

The polyurethane foam once rigidized has shown good resistance to a variety of chemicals. The number of chemicals tested was limited to chlorine, methanol, acrylonitrile, toxaphene (90% in xylene) and phenyl mercuric acetate (ammoniacal water solution). Only one material to date, methyl alcohol, has shown any adverse reaction. An evaluation of a broader spectrum of material appears warranted, however, to define the applicability and limitations of the foam. These tests should also include evaluation of the foam density. This property is determined in part by the degree of crosslinking and hydroxyl substitution, features which may be significant with respect to chemical inertness.

Towards the end of the initial program, two techniques were developed which markedly improved adhesion to surfaces wet with water. It is necessary to determine if these procedures are beneficial in situations where the wet surface is due to the spilled chemical. Sufficient testing should be conducted to define a procedure covering the broadest range of wet surface conditions. The selected procedure would then be incorporated into the portable unit, either directly into the chemical package or as an auxiliary unit.

Like the polyurethane, the testing of the chemical inertness of foamed concrete has been limited and a more comprehensive spectrum of materials should be examined. Foamed concrete does have the capability to dam flowing streams. The details for such emplacement varies with conditions and subtrate. Some further work appears warranted to determine the capability to place foamed concrete dams in existing bodies of water such as creeks, drainage ditches and the like.

The principal recommendation with respect to foamed concrete is the adaptation of generation to batch-type mixers. The majority of work to date has been performed with continuous mixers. These are more versatile than batch operations, but require level positioning and are not very amenable to inaccessible areas. Batch mixers have advantages in this regard. Some work has been performed to demonstrate feasibility. Difficulties were experienced in achieving the necessary control of materials' proportions. The development of the procedures using the batch type unit would allow flexibility in the selection between a continuous or a batch mixer to suit the topography and other conditions at the spill site.

The potential of soft detergent foam covers has been demonstrated on small spills in the laboratory and in a few isolated instances in the field. True proof of the advantages of such a cover requires much greater testing on large scale spills. Such parameters as rate of cover, adequacy of protection, rate of foam deterioration/rate of recover and atmospheric effects (wind, precipitation, etc.) must be measured.

The medium expansion imine modified system can be generated with commercially available generators. The low expansion pectin-fortified system has not lent itself readily to the common low expansion generators. It may be necessary to devise a generating system for application of that material. Foam pumps are a new item on the market that have the potential of handling the pectin system and should be evaluated before undertaking development of a new generating mechanism.

SECTION III

INTRODUCTION

It is immediately obvious in considering hazardous chemicals that the principal deterrent to the damage of the ecology from such materials is the strict control of their manufacture, storage and transportation. The first step, of course, is strict rules designed to prevent the spills of such materials. Even the most stringent rules, however, will not completely eliminate the possibility of accidental spills. Procedures must be available to control such discharges such that they cannot damage the surroundings or reach local waterways. Such control will be a major problem if such spills occur in the transportation mode. With land vehicles at least there are potential solutions which would tend to minimize, if not eliminate, the possibility of such spilled materials entering adjacent water systems.

In past efforts, the MSA Research Corporation (MSAR) has been associated with two programs to study the problems of hazardous chemical spills in unconfined areas. The first was concerned with the spill of liquid rocket fuels in field complexes[1], the second with spills or leaks of chemical warfare agents during transportation or in the field[2]. In both of these studies it was clear that immediate action had to be taken if there was any hope of containing or controlling the spill at all. Three basic steps were considered: (1) sealing of the leak if possible, (2) containment of the spilled material and (3) physical removal of the spill.

It was concluded from these studies that control of the spill of the hazardous chemicals from transporting vehicles must be considered as one major area in the prevention of hazardous chemical materials from damaging the water ecosystem. Based upon our prior work and our current knowledge in these areas, it was our belief that the available technology would allow the successful evolution of both portable and mobile systems which could provide surface containment of spilled materials at the site of the accident either by the formation of dikes or flow-diverting barriers. Technology was also available to provide in situ generation of surface covers to prevent vapor losses from such spills. Completely contained, the spilled materials can then be cleaned up by a number of techniques. Subsurface losses, seepage and the like, would require additional controls.

In considering the erection of dikes or diversionary barriers the initial thought is usually to natural materials. Although significant use should be made of natural barriers and depressions by diverting spills toward them, their use to construct dikes or other barriers pose a number of problems. Not all types of surface materials are amenable to the formation of dikes of any significant height. When the ground is frozen or water soaked, movement by hand is difficult if not impossible, and under the worst conditions even heavy equipment may not be sufficient.

To provide a general purpose system operable under all of the environmental conditions to be experienced, it becomes necessary to consider structures built up out of artificial materials. Whether these materials form an enclosure or divert the flow of spilled materials, the basic requirements are the same. Materials should be resistant to chemical attack, nontoxic, disposable and fire retardant if not inflammable. Most important, maximum benefit should be realized from as small an amount of material as possible using portable or mobile equipment with small power requirements.

In assessing the requirements, the limiting value would appear to be the necessity of obtaining large quantities of material rapidly from small portable or mobile systems. These conditions appear best satisfied by materials which can be foamed or expanded. At present two material classes possess the basic requirements. These are polymer foams and so-called foamed inorganic materials.

Although a large number of polymers can be produced in the foamed or expanded condition, only polyurethane appears to possess the necessary characteristics for field operable units. Formed by the exothermic reaction of two materials, the heat generated volatilizes and expands a reaction product or an added blowing agent which creates the foam. Polymerization occurs at the same time, setting the foam to a rigid mass. The only power necessary is pressure to expel and blend the two components. Other polymer foams require mechanical agitation and may be of open cell structure and thus form a porous medium.

There is a broad spectrum of inorganic materials which can be produced in lightweight form by blending them with a preformed detergent or protein foam. The major item in this class at the present is foamed concrete. Foamed gypsum is also an available material,as well as sodium silicate foam. The latter, however, requires mechanical agitation, is partially open-cell and subject to hydrolysis.

Once contained, rapid clean up of the spill is almost mandatory. Vapor release to the air and seepage into the ground constitute a significant material loss which poses immediate problems to the surrounding environment. Ground-water movement can transport spilled material into the water system.

Large exposed surfaces of spilled chemicals also pose an immediate threat, in terms of toxicity and flammability, to the personnel attempting to control and clean up the chemical as well as other individuals in downwind locations.

Isolation of the chemical surface along with control of boil-off would appear to be desirable. The surface covering should be such that it does not interfere with the clean up operation. In the past year foam has been shown to be effective as a surface cover to isolate and control vaporization rate of selected chemicals such as gasoline, ammonia and vinyl chloride monomer.

Based upon the existing technology, a program supported by the Environmental Protection Agency was undertaken by MSAR in four phases to evaluate and potentially evolve foam systems applicable to the containment of hazardous chemical spills. The first phase was concerned with polyurethane foam, the second with foamed inorganic materials, the third with rigidized high expansion materials and the fourth with soft foam covers. The following sections present a detailed reporting of the work conducted in each phase, the program accomplishments, and, where applicable, recommendations for additional work to further evolve the concepts.

SECTION IV

POLYURETHANE FOAM

One of the strategies for the control of hazardous chemical land spills depends on the availability of a small, portable system which could be carried on transporting vehicles and utilized by the carrier personnel. Polyurethanes, already commercially available as a portable foam dispensing system, potentially offered a quick response solution. Polyurethanes are resins derived from the catalyzed reaction between polyols and isocyanates. Once formed, they are reasonably inert to most other chemicals. The foamed form, which is currently used in a wide variety of applications, is obtained by blending a low boiling liquid, usually a Freon, into the reaction mass.

A typical portable, man-carried unit is shown in Figure 1. This is a packaged two tank unit. This size delivers some 10 cu ft of foam with an expansion of 25:1 and an output of approximately 1 cu ft/min. This unit would appear to be quite suitable to fill the requirement for a small, portable system to provide emergency diking. The only deficiency in the unit is the low output rate. A discharge of 4 to 5 cfm would be a more suitable situation for spill control. With the existing formulations and portable packages as a base, a program was undertaken to adapt this device for use in the control of hazardous chemical land spills. Three major items were considered:

1. Increasing the discharge rate to an average of 5 cfm.
2. Limited evaluation of the chemical compatibility of the urethane with hazardous chemicals.
3. Determination of the effectiveness of the material as a barrier against a variety of substrates.

System Output

The majority of current applications for urethane foam require a high quality material. To achieve this quality, it is necessary to obtain intimate mixing of the two components in the system just prior to discharge from the nozzle. The current design of the spray nozzle utilizes helical vanes within the body of the nozzle coupled with a small (1/32 in.) orifice. Although this is extremely effective in obtaining good mixing, it does severely restrict the rate of discharge

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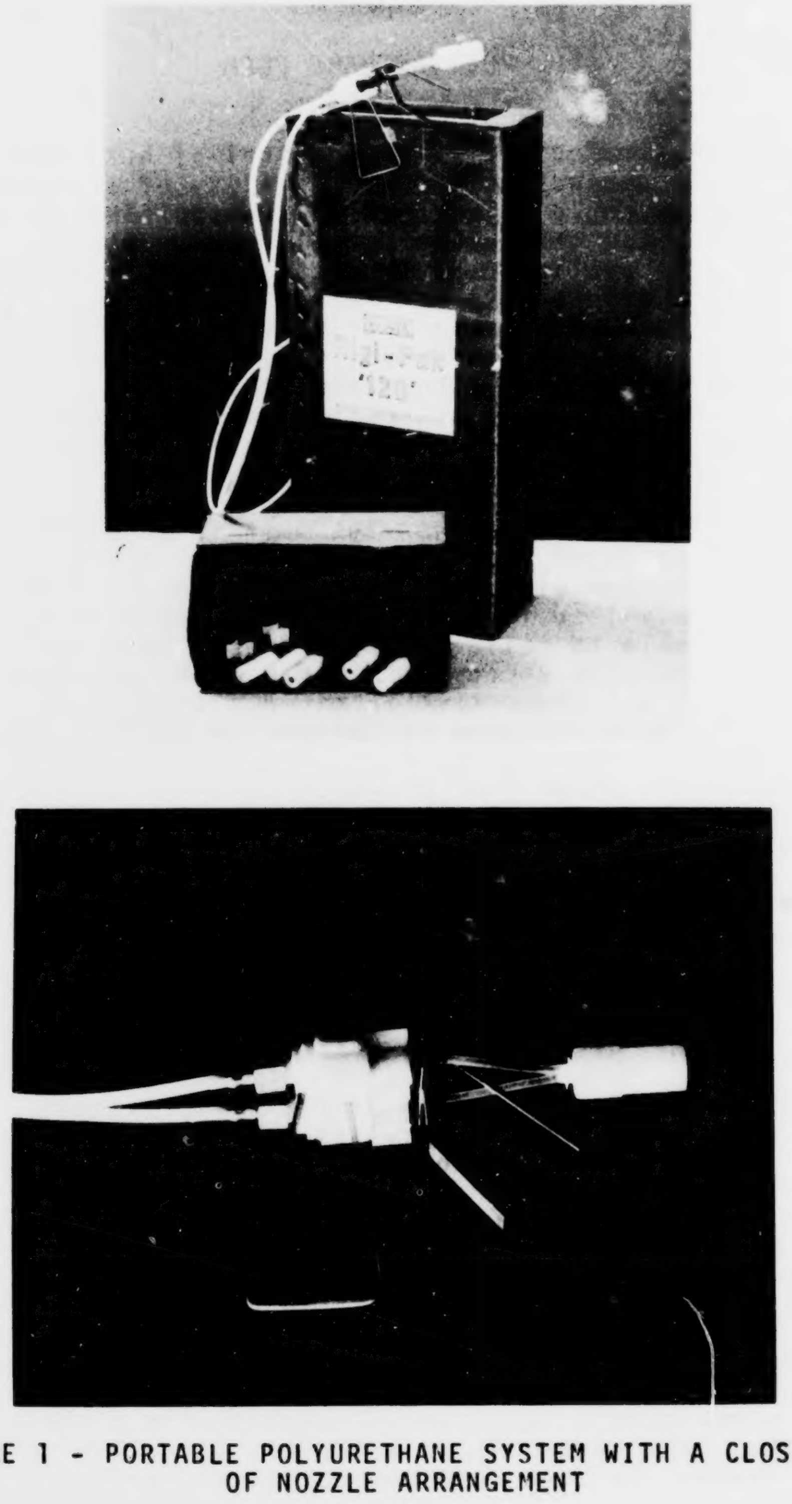
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FIGURE 1 - PORTABLE POLYURETHANE SYSTEM WITH A CLOSE UP OF NOZZLE ARRANGEMENT

of the urethane material. If the mixing helix is removed and the nozzle orifice enlarged to the maximum possible, which is some 7/64 inch, discharge rates averaging better than 7 cfm can be achieved, but the quality of the foam is reduced.

Current urethane systems use a combination of the blowing gas, usually Freon, and nitrogen to develop sufficient pressure within the system to discharge the two components through the nozzle. In the initial portions of this phase of work serious consideration was given to increasing both the quantity and the pressure of the nitrogen. Discharge rates which could be achieved in the absence of the mixing vanes raised the possibility that outputs in the range of 4-5 cfm could be achieved without the additional pressure. Increasing the nitrogen pressure would require increases in tank walls with an attendant weight increase. This is an undesirable situation where a man-carried package is concerned.

It was necessary to determine if the mixing system could be changed without reducing the quality of the foam to an unacceptable level. It was certain that the diking system did not require the foam quality of the existing applications, but poorly reacted material might lack the strength or chemical inertness to survive in the diking application. Two changes in the internals of the nozzle resulted in improved outputs with a foam quality which appeared to be more than adequate for the application. In one arrangement, the helix was shortened from its normal 50 mm to 35 mm to provide less resistance to flow. The resulting average output from the system was some 4 cfm. It is to be noted here that discharge rate of the package decreases with time due to the expenditure of the pressurizing gas; thus an average output of 4 cfm represents an initial discharge rate of the order of 7 cfm, decreasing to something less than 3 cfm as the final amount of foam is discharged. Other discharge rates show a similar variation.

The second arrangement which gave a slightly poorer quality foam but an average output in excess of 5 cfm involved removing the helix completely and replacing it with a double cone. This provided a second orifice within the body of the nozzle by narrowing the inside diameter of the nozzle from 16 mm to 4 mm over a 55 mm length.

When the 5 cfm average output was achieved, work on improving the system output was terminated. Determination of which of the two arrangements was acceptable could only come from field studies which would provide a practical evaluation of the quality of the foam being produced. These field studies have shown that both arrangements are acceptable. The double cone system was selected because of its slightly higher output rate.

Foamed Barrier Studies

Concurrently with the previous studies, work was initiated on evaluating the ability of the urethane foam to bond to a variety of substrates and to contain a significant liquid head. This work was initiated before full evolution of the portable unit since it was felt that the bonding ability and ultimate strength of the foam were reasonably independent of the rate of generation.

A variety of natural substrates ranging from bare ground to dense growth were available for evaluation along with gravel and paved surfaces. To provide a broader spectrum of conditions, however, two additional installations were fabricated. The first was a concrete pad incorporating a typical curb type drain; the second was an asphalt surface incorporating a highway storm grate. This facility is shown in Figure 2.

The initial work was with hard surfaces -- asphalt, concrete, and hard packed dirt -- and significant success was realized in applying the urethane and successfully containing significant volumes of water 2 to 3 ft in depth. A circular form of polyurethane 36 inches high and 30 inches inside diameter was set up on concrete and maintained full of water without leakage for a period of days. Similarly, polyurethane was used to block the curb drain set in concrete as shown in Figure 3. Sealing to asphalt was as good if not better than sealing to the concrete.

Similarly, effective seals could be accomplished against bare ground. The ability of the polyurethane to dike liquids in that particular situation, however, depended upon the integrity of the bare ground. A breach of the dike eventually occurred. The breach was always in the substrate just below the level of the urethane dam and usually restricted to a small localized area. The time required to achieve the breach was a function of the head of water and the density of packing of the substrate. Even though the dike was eventually breached, several inches of water could be held for an hour or more. In the case of bare ground, where poor containment was experienced, additional downstream dikes could be erected to extend the control time of the liquid material.

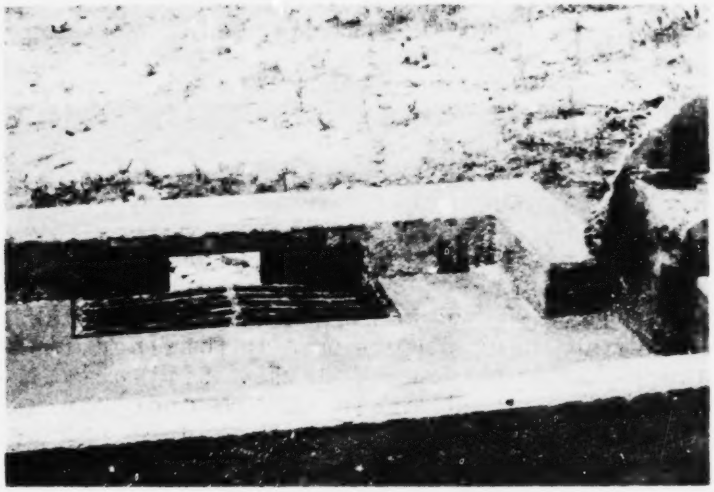


FIGURE 2 - CONCRETE PAD WITH CURB DRAIN

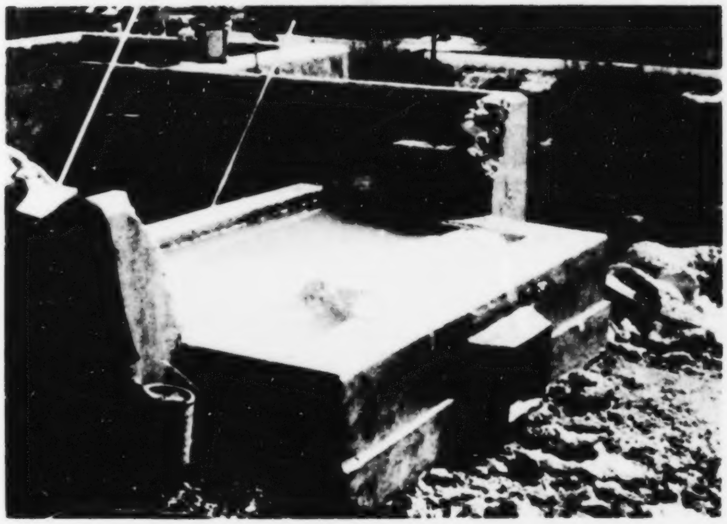


FIGURE 3 - POLYURETHANE BLOCK OF THE CURB DRAIN

As the test sequence moved from dry bare ground to gravel, vegetated areas and wet surfaces, the effectiveness of the urethane as a liquid dike diminished rapidly. With wet surfaces the problem was lack of adhesion and with the gravel and the vegetated ground, the inability of the urethane to penetrate more than a few fractions of an inch below the top surface.

The difficulties of bonding urethane to wet surfaces proved to be a major difficulty and is discussed in a separate section of this report. The inability of the foam to penetrate very far into porous or vegetated surfaces proved more amenable to solution. In polyurethane technology, the term "cream time" is used to denote that interval between the mixing of the chemicals and the onset of foaming. In normal formulations, cream time varies between 2 and 4 seconds. This means that some frothing has already begun as the material leaves the nozzle. As frothing proceeds, material viscosity increases, thus as the material strikes the surface it does not have the fluidity necessary to penetrate and tends to bridge across the high points.

Cream time can be varied by changing the reaction rate and/or the volatility of the blowing agent. Such variations were studied in the program. It was found that significant changes were possible which provided not only for a higher expansion of the urethane without significant loss of its other desirable properties but that variations in cream and rise time alleviated the difficulties initially experienced with gravel and vegetated surfaces.

By making minor changes in the catalyst from triethylamine (TEA) to dimethylethylamine (DMEA) and a major change in the blowing agent from a Freon type material to methylene chloride, a rigid polyurethane foam was achieved with a density between 0.5-0.6 pcf rather than the normal 1-2 pcf. The rise time of this particular form of polyurethane foam was much more rapid than that of normal materials but the cream time, that interval before the onset of foaming, was increased to some 12 to 14 secs from the normal 2 to 4 sec increment. It is this last feature which allowed a better penetration into vegetated surfaces and gravel.

This particular system had one apparent drawback. Because of the exceptionally fast rise and the concentrated heat release, there was a tendency of the foam to shrink slightly upon cooling from the reaction temperature. Field tests, however, showed that the bonding strength to dry surfaces of concrete, asphalt and bare ground was sufficient that the shrinkage did not adversely affect the material's ability to contain liquids. Further, the cream time was sufficiently long that penetration did occur into vegetation to the point that effective seals could be achieved against the surface as long as the vegetation was not too thick and matted. Improved penetration was also achieved on gravel surfaces but never to more than some 2 diameters of the stone. It is doubtful if this material could be effectively utilized to control liquid spills on a gravel surface.

The benefits due to the increased expansion and the extended cream time of the new formulation without sacrificing any of the desirable characteristics exhibited by the normal 1-2 pcf foam led to the adoption of this particular material as a standard material in this phase. The use of methylene chloride as the basic blowing agent produced some changes in materials viscosity. To maintain the 5 cfm delivery rate, and to get good mixing in the nozzle of the correct proportions of both resin and activator, minor changes were necessary. To achieve the desired 1:1 resin-activator proportions, the cross-sectional area ratio of resin and activator orifices was changed to 2.3:1. Some mixing problems were encountered but were overcome by adding 10% by weight of Freon R12 to both resin and activator. Volatilization of this material in the nozzle provided for good mixing. With the Freon-nitrogen pressure system, 200 psi had to be used as the initial tank pressure. With the methylene chloride, the pressure was increased to 220 psi.

A significant number of field studies were run using this material on a variety of substrates to block and hold water with good results except when wet or extremely cold surfaces were involved. Figures 4 and 5 show dams erected with this type of polyurethane material. By expanding this material into a rubber or plastic envelope it was possible to block water flowing in culverts and other similar circular drains.

The final effort in this portion of the program was an evaluation of the ability of the polyurethane materials to block or divert already flowing streams. These efforts were completely unsuccessful. The primary difficulty was the inability to achieve good adhesion between urethane and a surface wet by water or one of the hazardous chemicals. Several mechanical aids were tried, such as the use of hold down stakes; heavy filler, such as rock; or a support system such as screen or netting. None of these were successful in improving the ability of the polyurethane to combat the flowing stream situation. In addition, they complicated the construction of the dam appreciably. This is a major disadvantage when it is considered that the portable unit must

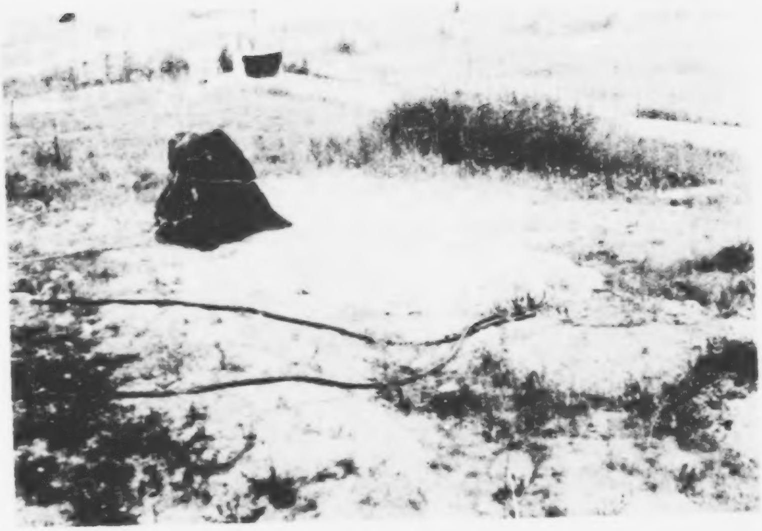


FIGURE 4 - SINGLE POLYURETHANE DAM SET ON BARE GROUND

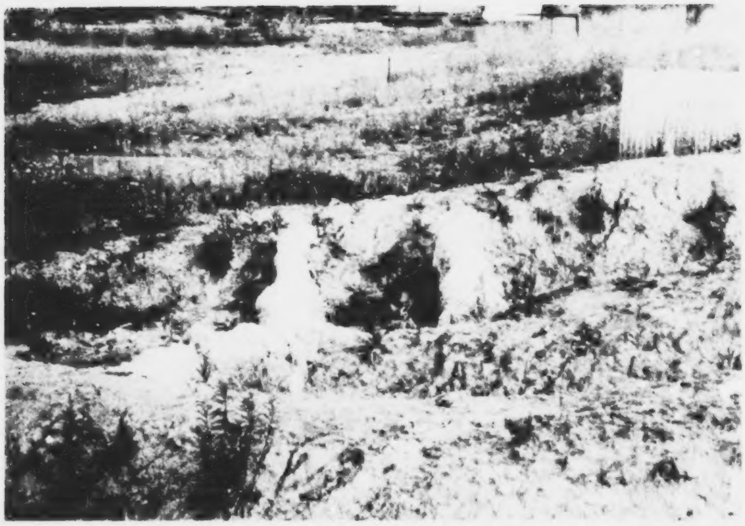


FIGURE 5 - DOUBLE POLYURETHANE DAM SET ON BARE GROUND

be designed to be used by essentially untrained people in emergency situations. Work in this area was thus terminated.

Chemical Compatibility

All existing data would indicate that polyurethanes, once rigidized, would be essentially inert to a majority of the long list of chemicals now appearing in the hazardous chemical classification[3]. The substantiating data is relatively meager, however, and it appeared necessary to conduct some tests with representatives of several classes of materials which had a high order of ranking in the current listing of transported hazardous materials. In addition, there is a question as to the effects the hazardous materials might have on the reaction and rigidizing of urethane foam. Thus, tests were necessary in this regard, also.

Five chemicals representing types of hazardous chemicals shipped in large quantities in the United States were selected for reactivity tests. These were chlorine, methanol, acrylonitrile, toxaphene (90% in xylene) and phenyl mercuric acetate (ammoniacal water solution). With the exception of methanol, none of these materials exhibited any significant reaction with the urethane foam once it had rigidized. Methanol did not react but tended to be absorbed by the foam. Tests on a large scale which were conducted as part of the study of blocking flowing streams, verified the laboratory findings.

The foam behavior with methanol is not understood. It is not a destructive reaction but rather one of absorption. The absorbed methanol does destroy foam rigidity, however. Tests run with acetone, a polar compound like methanol and acrylonitrile which is also polar in nature did not produce this effect. Further work is necessary to explain the phenomenon and to define what other materials might behave as methanol. At the present, polyurethane is not recommended for containing methanol.

To determine the effect of the hazardous materials in their liquid form on foam generation and rigidizing, a second series of tests were run where foam was generated directly into a pool of each of the chemicals. In each case there was a reaction between the urethane and the hazardous chemical. It was never violent but it destroyed the urethane before it could foam and rigidize.

To assess the effects of the hazardous chemicals' gas phase, foam was applied to the edges of a tray 10 in. x 10 in. x 4 in. holding the chemical. It was possible for the urethane to set up and bridge each of the chemicals, with the exception of chlorine. It can thus be concluded that vapors emanating from the chemical were not sufficient to impede urethane formation. In the case of chlorine and ammonia the heat of urethane reaction produced rapid boiling. Even with boiling, the ammonia pool was covered and even an hour later there was still liquid ammonia in the bottom of the tray. With chlorine, however, the issuing vapors kept a blow hole open in the urethane cover until all chlorine had been vaporized.

A much broader range of chemicals needs to be evaluated, but on the basis of this limited data it would appear that urethane foam can control spills of a variety of hazardous chemicals. It is not feasible to generate foam directly onto the spilled materials but vapors in the surrounding area will probably not have any significant effect on the generation or set of the foam.

Adhesion to Cold, Wet or Contaminated Surfaces

The degree of success achievable by any hastily erected barrier is directly linked to the ability to anchor the barrier to the existing surfaces. As has already been explicitly stated, in its present state of development a urethane type formulation is not practical on wet or contaminated surfaces. Cold surfaces also pose a problem but of a lesser magnitude. The presence of water, alcohol, etc. act as chemical interferants and disrupt the stoichiometry of the applied urethane mix. Oil-like materials, merely because of their physical presence, block any interaction with the surface. Cold surfaces interfere with the exotherm necessary for foam formation. A specialized effort was directed to solve the problem of anchoring urethane to water wet surfaces. Some degree of success was realized but time did not permit an extensive development program. The temperature problem received only a cursory investigation and also needs more work.

Wet Surfaces

Four approaches were taken in an attempt to alleviate the poor adhesion to wet surfaces. The word poor is used because there was always some attachment of the foam to the surface. Adhesion was quite discontinuous, however, with those areas of attachment exhibiting only a weak bond. The problem had been determined to be interaction between the isocyanate and the water to form CO_2. This generation of gas at the immediate surface retarded adhesion. Reaction was not restricted to the surface. Water tended to flow upward, probably as a vapor, into the foaming mass. The further reaction in the foam created gross voids which were the areas of no attachment.

Tests using wet surfaces were performed in the laboratory in a rather expeditious manner. Patio block concrete was used as a substrate. Water was added to the test area insuring complete coverage. The test surface was then tilted to allow excess water to drain free. This method insured a saturated area without pools of liquid. A total of about 20 cc of urethane mix was prepared including any additives under study. For comparison, a test was also made in the immediate area using the base formulation alone. All solutions were hand mixed and poured onto the test area.

The first approach was a flash coat of isocyanate to consume the water. A reaction occurred but the material formed had no integrity and blocked any possibility of adhesion of the following polyurethane foam to the substrate test pad.

The second approach involved the addition of a number of materials into the base formula to combat the water. These chemicals are listed in Table 1. They represent three classes of materials: (1) nonionic wetting agents to improve spread and penetration of the foam and increase strength of adhesive bonding; (2) water soluble polymers to occlude the water; and (3) gelling agents to perform essentially the same task as (2). This total approach was taken on the basis of empirical data emanating from the high expansion materials phase, where such materials added to the water side of the isocyanate-water system showed some improvement in that material's adhesive quality. With normal urethane none of the additives exhibited any improvement.

TABLE 1 - ADDITIVES TO THE BASE FORMULATION

Nonionic Wetting Agents	Water Soluble Polymers	Gelling Agents
Triton X-100	Acrysol GS 1607	Primafloc
Polyethyleneamine	Rhoplex LC-40	PVA (72-60)
	Amisol	Carbopol 941
	Dow Latex 460	Acrysol ASE-60
	PVA (72-60)	Hycar 1571
	Gantrez AN-139	

The third approach was the use of drying agents and sorbent materials as a precoat on the wet surface before the application of foam. These materials listed in Table 2 were spread as a thin dry layer on the wet block. They were effective in tying up liquid water on the surface, but could not effectively remove surface adsorbed moisture.

TABLE 2 - SELECTED CHEMICALS APPLIED AS A PRE-COAT
FOR SORPTION OR DRYING

Ethyl silicate

Organic ammonium silicate

Calcium chloride

Calcium sulfate

Drysorb

The fourth approach consisted of a pre-coat of the catalysts, either TEA or DMEA. With both of these materials, excellent adhesion was achieved. The reaction involved is probably between the water and isocyanate and parallels that action hoped for in the first approach. The excess catalyst present due to the precoat restricts reaction to the immediate surface with no gross voids formed nor prolonged CO_2 generation to adversely affect the initial adhesion developed.

The success using a precoat of TEA was further verified by field tests run on the concrete pad previously described. The tests revealed an impediment in the bonding action. A barrier formed in this manner was ineffective in holding water for any significant period of time. It was concluded that the excess catalyst at the surface resulted in a foam containing an inordinate amount of water soluble products such as amines. These products were slowly leached from the foam by the solubilizing effects of the water. This erosion of the foam structure by water eventually caused barrier failure. Limited tests were made involving the addition of materials which would contain or otherwise protect the soluble fraction, but no progress was realized before the end of the program. A change in the catalyst or the use of a material which would render the products insoluble could possibly alter the situation.

Cold Surfaces

The evaluation of the effect of temperature was primarily limited to substrate temperatures. Urethane systems are normally recommended for a 50°F or better storage and use temperature. Results with lower test temperature will be discussed in the section on storage.

Polyurethane foam, both normal and low density, is capable of containing low boiling liquids such as ammonia and chlorine if the dike or seal is erected at surface temperatures 50°F or above. The erection of polyurethane barriers at lower temperatures is known to suffer since the substrate temperature robs the reaction exotherm.

A series of barriers were erected on the concrete pad with the curb drain during the winter months. As the substrate temperature decreased, the expansion of the initial layer of urethane foam decreased, the expansion of the initial layer of urethane foam decreased, as did the strength of the interfacial bond. The bond was always strong enough to block liquid flow, but it tended to leak. Temperatures as low as 15°F were encountered during the sequence. There was no correlation between the temperature and the rate of leakage.

In an effort to improve bonding to cold surfaces, catalyst changes were made to accelerate the reaction and concentrate the heat output. Of the materials tested, an addition of 0.10% lead napthanate had the best effect. It decreased the cream time to some 3 seconds at temperatures as low as 15°F.

The accelerated reaction improved expansion and bonding at low substrate temperatures. It was detrimental, however, with respect to the ability to penetrate into vegetated surfaces. Thus, at the present state of development, a choice must be made between the ability to achieve good bonding to a cold substrate or a vegetated one.

Storage Tests

At the termination of that portion concerned with polyurethane, three short term storage cycles were initiated. Two storage tests were at room temperature (75°F) and one at 40°F. As expected, the lower temperature storage adversely effected the expansion of the foam as well as increasing the cream time. It was decided that lower temperatures would only exaggerate the situation. Since time was not available to do more than had been accomplished with the lead napthanate, work was terminated.

The initial tests at ambient were conducted over a six week period. No change was noted in the materials or the foam generated from them until the sixth week. At that time separation had occurred in the resin mix with two liquids formed. They could be reblended by agitation but separated again within 24 hours. Since the only major change that had been made in formulation was the methylene chloride, that was assumed to be the contributing factor.

A second test package was made in which the methylene chloride was added to the activator instead of the resin. Eight weeks of storage with this arrangement showed no problems.

With methylene chloride in the activator changes in the delivery ratio of materials was necessary from 1:1 to 1.3:1 activator to resin. At this ratio good quality foam of an average density of 0.6 pcf could be obtained at an average rate of 5 cfm.

As the final step in the "polyurethane foam" phase of the project, two units using the methylene chloride formulation and the foregoing mixing arrangement were shipped to the Technical Project Officer. One was the refillable laboratory unit and the other a non-rechargeable portable unit typical of that to be expected as a commercial unit. The refillable laboratory unit has a capacity of 2.1 gallons and delivers 25 cu ft of foam. The typical delivery rate versus time curve is shown in Figure 6. The prototype of the commercial unit has a total material volume of 6.4 gallons and delivers approximately 65 cu ft of foam at 5 cfm. The initial nitrogen pressurization is 220 psi with some 10-15% ullage. The total weight of the system including the carton is 65 lbs.

The prototype urethane package can be activated by opening the two flow-control valves. Triggering of the main valve at the nozzle disperses the foam which initially will appear as a free flowing liquid.

Polyurethane foam will serve a number of functions such as construction of barriers, diverters, plugging of sewer drains, covering storm drains and damming of drainage ditches, etc. The single factor which will exert the most influence in determining the usefulness of foam will be the type of surface. On dry, firm surfaces such as concrete and asphalt and at temperatures above 30-35°F no difficulties should be experienced. On this type of substrate tests have shown that 4 foot high barriers can easily be constructed in which at least a 3 foot head of water can be contained. Surfaces which are cold and/or wet (water, solvents, etc) will impair the quality of the initial deposit of foam. This layer of low quality foam can serve as a buffer zone upon which additional foam can be successfully applied. Unfortunately, cold, wet surfaces impair the bonding or adhesion and the

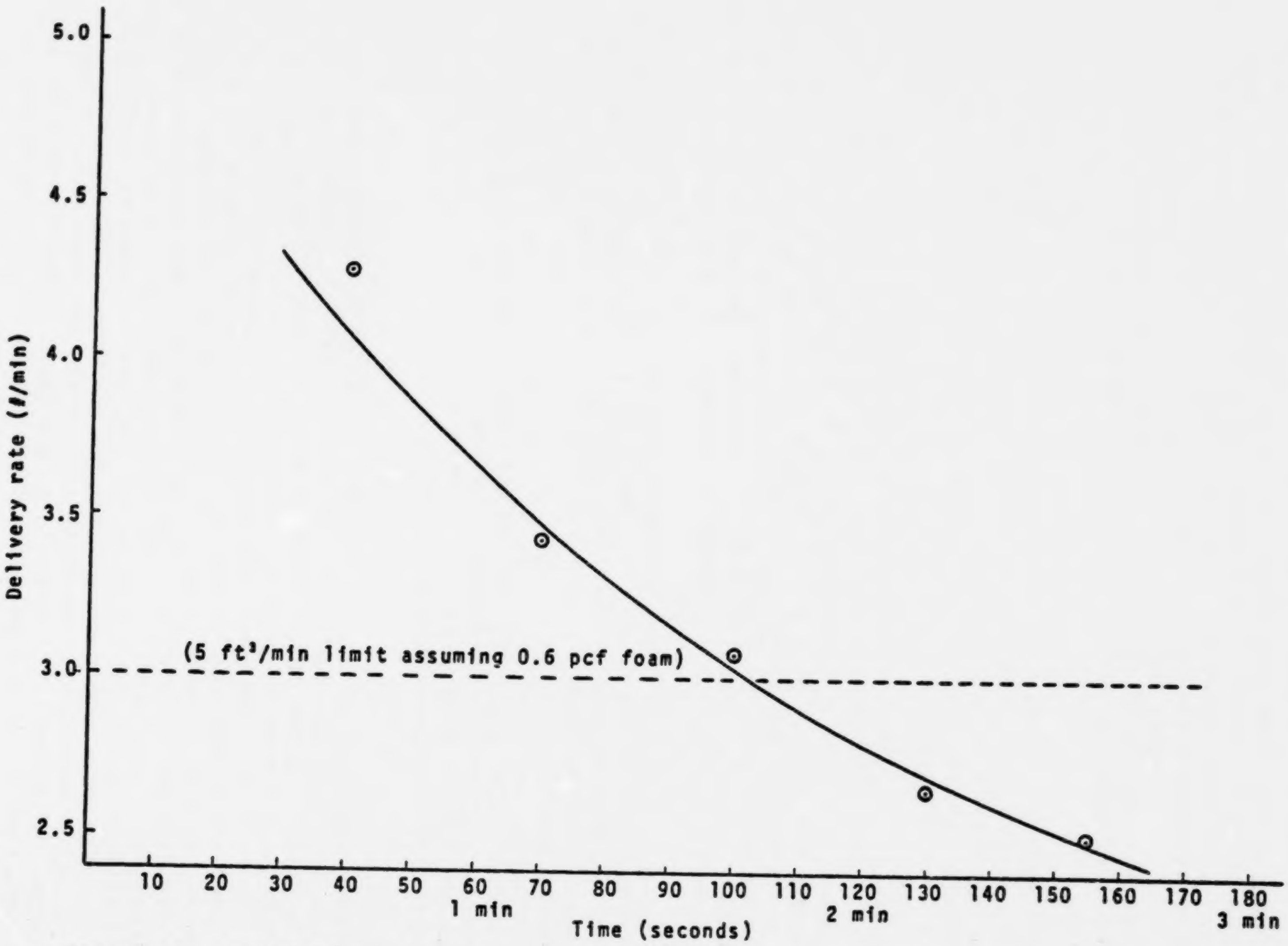


FIGURE 6 - TYPICAL TIME VS DELIVERY FOR 0.6 PCF POLYURETHANE FOAM SYSTEM

low quality foam which results is prone to leakage. Grassy and weedy surfaces also prevent the penetration of the foam and thus the formation of a good seal. Leak-plugging and strengthening can be achieved to a certain degree by selected addition of more foam, but in general the performance of barriers built on this type of surface is unpredictable and most frequently merely limit the flow of liquid.

The volume of foam available in a single unit may not be capable of impounding material volumes carried by current transportation vehicles. Sixty-five cu ft of foam can form a barrier 1 ft high by 1 ft wide by 20 ft in diameter which would impound some 2000 gallons. Reducing the height to 6 inches would increase this to 4700 gallons. The 12 inch base is necessary for good strength on the substrate. The primary function appears to lie beyond full impoundment. There is sufficient material in 65 cu ft to be successfully used as a flow diverting barrier to direct the spilling chemical away from a water system and/or into a naturally occurring or otherwise available collection site. It can be used to supplement these areas into more effective impoundment. Where leaks are slow it can provide impoundment until more effective equipment can be brought to the site.

In many cases spilled material ends up following existing courses to water systems. The foam is able to effectively seal sewer openings and storm drains to prevent the chemical from entering the water system in that way. On major highways and railroad right-of-ways drainage paths including ditches, culverts and conduit are used to divert and drain water. The specified volume of foam is capable of sealing these paths to effectively contain the spill. There are examples of chemical spills which have entered urban sewer systems or have reached rivers by flowing through railroad drainage systems.

The chemicals which can be controlled by urethane foams need to be clarified further. Data on specific chemicals is limited. Water based liquids with the exception of strong acids are contained as are nonpolar organics. Data is also positive for chlorine and ammonia. Polar solvents are a question. Acetone is controlled but methyl alcohol is not. If the foam is applied and rigidized prior to contact with the spilled chemical, it is doubtful that any catastrophic reaction will occur. Reacting chemicals can break bonds destroying the adhesion to the surface or they may even seep through the foam mass as is the case with methyl alcohol. Thus in most cases urethane will exercise some control if applied correctly. Even in those cases where control is not effected it is not expected that the spill situation would be exaggerated. Guidelines in this general area are almost completely lacking, however.

SECTION V

LOW-EXPANSION INORGANIC FOAM

The objective of this phase of the program was "to evaluate and develop current expanded inorganic materials such as foamed concrete as barrier-forming materials for containing hazardous chemical spills".

Foamed concretes and foamed gypsums are common materials of construction, with well developed formulation and application technology. To use these foams for spill containment, it was necessary to provide them with instant setting capabilities which allow barriers to be built up without forms. To accomplish this, it was considered necessary to impart a gelling action to the foamed material as it was delivered to the barrier location. Thus, the basic mechanism to be evolved was a gellant system to provide a uniform, semirigid foamed mass to standard foamed concrete and foamed gypsum mixes.

Assuming success in this regard, optimum gellant systems would be defined along with the associated concrete or gypsum formula. These compositions would be examined for their ability to block and hold spills of hazardous chemicals, along with the ability to form structures of appropriate shapes and heights. The ultimate system would then be demonstrated in the field.

Foamed concrete is one type of lightweight concrete. It is an established construction material with a density range usually given as 25 to 100 pcf. (More recently the American Concrete Institute (ACI) has defined the density range of 50 pcf or less to be low density concrete.)

Lightweight concrete can be either precast, or cast-in-place. Its largest use is in industrial and commercial buildings where field placed, low density concrete is commonly used for fills, thermal insulation and roof decks.

Because of the basic behavior characteristics of these concretes under impact and shock loading, they have military applications as shock dissipators in protective construction schemes.[4] They are also being considered in a number of new non-military applications.

Foamed concrete is produced by introducing controlled quantities of air, water and foaming agent under pressure into a foam nozzle and blending the resultant foam with cement slurry or cement-aggregate slurry in a variety of mixing devices, either batch or continuous. The foam must have sufficient stability to maintain a structure until the cement sets to form a matrix of low density concrete. Foam generation and proportioning into the cement slurry are regulated to achieve control of final strength and density. Up to 80% of the final mix volume may be air, added as pre-formed foam. The resultant foamed product can be pumped distances up to 1000 feet, to a height of 300 feet. The pumping parameters are simply a function of the slurry viscosity, pump specifications and slurry set time.

Existing foamed concretes have similar fluidity and set times as normal concretes and thus require forms. There are, however, a number of fast set gypsum and concrete formulations which have never been formulated in the cellular, or foamed mode. REG-SET, a commercial fast set concrete, for example, can reportedly be made to take its set within 5 minutes after mixing with water . "Hardstem" and "Hardstop", both gypsum formulations, were developed as rapid set formulations by the British for pour-in-place mine bulkheads.[5] More recently, Halliburton[6] developed both fast set gypsum and concrete-based formulations in their investigation of materials suitable for sealing abandoned mines to prevent acidic mine drainage. Various additives and sodium silicate were employed to achieve extremely rapid sets. This latter work, although employing normal density materials, provided a suitable basis for our study of foamed materials. Our program consisted of:

1. Preliminary formulation evaluation
2. Small-scale barrier pours
3. Field testing

Each of these areas are discussed in detail in the following sections.

The objective of this laboratory study was to develop leads for possible formulations or techniques that could be developed into an instant-set pour system with slurry mixing equipment. Therefore, commercially available slurry mixing, preformed foam and pumping equipment were employed without modification in order to expend more effort upon the formulation development and the feasibility of the technique as a spill control measure.

Preliminary Evaluations

The evaluation studies were conducted on a small scale, on the order of 1/4 to 1/2 lb of material per experiment. Studies with gypsum formulations considered accelerators and gel-set formulations employing the water soluble polymer polyvinyl alcohol (PVA) and a gelling agent.

Similar studies were also conducted on two fast-set cement formulations developed by Halliburton Company. One of the Halliburton formulations consisted of a mixture of cement, bentonite, fly ash and gypsum. It employed bentonite to obtain high viscosity and gypsum to obtain a fast set. A second, more rapid-set formulation, employed cement and bentonite for structural strength and sodium silicate to impart the rapid set to the mixture. A specialty gypsum (Hydroperm) and a regulated-set cement (Huron Cement Company)[7] were also investigated.

Table 3 summarizes our studies to accelerate the set of gypsum using an accepted accelerating agent (Na_2SO_4) at several concentration levels. Set times were reasonably rapid when compared to normal plaster formulations. However, when using larger amounts of sodium sulfate, the time to set was not nearly fast enough for this intended application.

TABLE 3 - SUMMARY OF THE EVALUATION OF THE SET OF GYPSUM FORMULATIONS* WITH ACCELERATORS

Quantity of Na_2SO_4	Remarks
none	all blended at once - 7 min.; resistance to flow, 10 min.; jello-like; 21 min.; set.
0.6 g	gypsum slurried with 62 g H_2O and blended with foam from remaining ingredients - 6 min.; heat but not set; 17 min.; no structural integrity, plaster set in little balls.
0.8 g	all blended at once - stirred 1 min.; 2 min.; no flow; 4 min.; lost sheen; 7 min.; hard set.
1.6 g	same as above - no flow in 2 min.; set in 4 min.

*Standard mix - gypsum, 100 g; water, 77 ml; protein concentrate, 0.6 g

TABLE 4 - SUMMARY OF THE EVALUATION OF PVA-GELLED GYPSUM SYSTEMS

Gypsum (g)	H_2O (cc)	PVA (cc)	Foam or Foam Concentrate	Gellant	Remarks
100	72	3	0.6 g protein conc.	sat'd-$Na_2B_4O_7$ soln.(4 cc)	stirred 1 min. - no foaming action; added $Na_2B_4O_7$ soln., stirred 1 min. giving rubbery mixture; 8 min. lost sheen; 16 min., hard set.
100	57	3	2 cc MSA conc.	-	no foaming action on vigorous stirring.
100	72	2	2 cc protein conc.	sat'd-$Na_2B_4O_7$ soln. (2 cc)	stirred 1 min. - poor foaming, added $Na_2B_4O_7$; 7 min., no flow; 15 min., friable but set; 1 hr., tough, hard structure.
100	72	2	2 cc protein conc.	Congo Red 0.3 g	stirred 1 min. with 37 cc H_2O - added congo red in 35 cc H_2O; approx. 50% increase in vol. (20% of expected use); 2 min., still flows; 11 min., set.
100	74	(combined into preformed foam)		Congo Red 0.8 g	slurried ingredients would not blend well with preformed foam.
100	(combined into preformed foam)			Congo Red 1.0 g	formed foam gypsum of reasonably light density- 14 min., no flow
200	(88 g of preformed foam with PVA)			sat'd-$Na_2B_4O_7$ soln. (4 cc)	stirred 1 min. after adding $Na_2B_4O_7$ to give viscous mixture; 3 min., set; 12 min., hard.
100	(80 g of preformed foam with PVA)			sat'd-$Na_2B_4O_7$ soln. (2 cc)	same as above, but PVA gel appeared to separate - no structural integrity.

The gel time for polyvinyl alcohol-containing gypsum formulations was also slower than desired (Table 4). Polyvinyl alcohol solutions can be gelled to a rigid structure with basic materials such as borax, and various dyes such as Congo red. Although we obtained some highly viscous mixtures by adding small amounts of saturated solutions of $Na_2B_4O_7$ to slurries containing polyvinyl alcohol, at no time did we feel that the time to set was short enough to allow us to build barriers of practical heights.

Our evaluation of the cement-gypsum formulation developed by Halliburton Company was initially encouraging, but failed to develop into a practical fast-set system. The formulation, as developed, is a two-slurry system; one containing cement, fly ash and water; and the other, gypsum and bentonite. In Halliburton's application, the bentonite-containing slurry is premixed to allow the bentonite to hydrate before mixing with the cement-fly ash slurry. Our initial experiment conducted in this manner was encouraging (Table 5); the formulation resisted pouring after only one minute and took a hard set after five. For the intended emergency spill control application, however, the two-slurry system was complicated and time consuming. Thus, our efforts were

TABLE 5 - SUMMARY OF THE EVALUATION OF CEMENT-GYPSUM* SYSTEMS

Type of System	Initial Set-Time (non-pouring)	Set-Time
(1) two slurry	1 min	5 min
(2) single slurry	4 min	9 min
(3) single slurry with REG-SET cement	5 min	15 min
(4) single slurry with added K_2SO_4 (2.5 g)	2 min	5 min
(5) single slurry with added K_2SO_4 (5.0 g) plus protein foam	4 min	5 min

*Standard mix - cement, 20 g; gypsum, 40 g; bentonite, 4 g; fly ash, 40 g; water, 62 ml.

directed toward using this formulation compounded as a single slurry system, without prehydration of the bentonite. As noted in the second experiment, the time to a non-pouring formulation increased from one minute to four and the hard set time from five minutes to nine.

No particular improvement was noted in Run (3) when the fast setting REG-SET[7] cement was substituted for the Type I Portland cement used in the first two experiments. This was not too surprising since REG-SET cement, although much faster setting than the Type I cements, will not normally set before five minutes. Adding potassium sulfate as an accelerator to the REG-SET cement did not appear to materially aid the initial set; however, once initiated, a hard set rapidly developed.

The last experiment (5) was somewhat encouraging in relation to our ultimate goal. Protein-based foam was added to the slurry to achieve a final wet set density of 35 pcf without significantly altering the set time of the mix. Unfortunately, none of the above formulations set fast enough for our application, but this experiment gave hope that if a fast set mix could be developed, the addition of preformed foam to achieve the desired low-density barrier material would not affect the set time.

Our most encouraging result came from a modification of another of Halliburton's specialty formulations developed for sealing mine entries (Table 6). This system was also a two-slurry formulation containing water and cement in one slurry, and a water, bentonite, sodium silicate mixture in the other. As mentioned previously, we felt that the two-slurry system was not practical for our application, but that the addition of a solution of sodium silicate to the foamed cement formulation as it exited the nozzle was entirely feasible. We anticipated forming a lightweight slurry of cement, bentonite, water and preformed foam, and adding the silicate solution by means of a water ring at the nozzle to achieve a fast set.

Our initial laboratory scale studies (runs 1-4) were discouraging until we discovered that gel formation occurred within seconds after adding the sodium silicate (run 5), and that any additional agitation only served to break up the exiting gel. Once formed, the gelled material resisted flow and appeared to have reasonable strength. In addition, preformed foam made from MSA salt water foam concentrate was compatible with the cement-bentonite mixture and encouraging samples of foamed concrete of 37 and 45 pcf were obtained (runs 6-7).

TABLE 6 - SUMMARY OF THE EVALUATION OF CEMENT-SILICATE SET SYSTEMS*

Run No.	Preformed Foam Added (cc)	Gel Time (seconds)	Cement Density (pcf)	Remarks
1	---	5-10	--	Components slurried, silicate added while stirring.
2***	---	5-10	--	Same as above
3	---	--	--	MSA salt water foam concentrate (2 cc) slurried with components; expanded 2 times original volume.
4	600	--	--	Preformed foam mixed with slurry, silicate added while stirring, weak gel structure.
5	400	--	--	Same as above; gelling occurred before complete addition of silicate, additional stirring broke up gel.
6	400	2-3	37	Slurried to about 800 cc, silicate added all at once while stirring.
7	400	2-3	45	Slurried to about 650 cc, silicate added all at once while stirring.
8**	500	2-3	--	Slurried to about 750 cc, silicate added all at once while stirring.

* Standard mix - Portlant Type I cement, 192 g**; bentonite,11 g; water, 189 ml.

** 192 g of solids in Run 2 made up of cement (20 parts), fly ash (40 parts), gypsum (40 parts).

*** Mix contained 231 g of Portland cement.

Experiment 8 summarized in Table 6 was an attempt to determine if the cement-fly ash-gypsum formulation evaluated in Table 5 would also gel with sodium silicate. This was found to be the case.

Small Scale Barrier Pours

Small scale barrier pours using field-scale equipment were conducted using a Mason Flow Mixer, a continuous slurry generator developed by Hoge-Warren-Zimmerman of Cincinnati, Ohio and a Model 2000 Slurry Rock Dust Distributor, a batch slurry mixer manufactured by MSA for use in coal mines. The formulation development work and pouring techniques were developed with the Mason Flow Mixer.

The Mason Flow Mixer is shown in Figures 7 and 8. The unit consists essentially of a hopper for powdered solids, a screw feed for solids metering, a slurry chamber and a slurry pump. For producing foamed products, preformed foam is added either in the slurry pump or immediately downstream of the slurry in the delivery hose.

The unit is capable of producing slurry in the range of 5-10 gal/min. It requires 220 V power and a water supply, but can also be powered by a gasoline engine. This particular unit is adapted for laboratory experimentation. Controls are available to vary the water-to-dry powder ratio, the rate of slurry production, and the speed of the slurry pump. On-off controls for the water and powder feed as well as automatic wash out capabilities are available on a remote control, hand-carried push-button device.

In operation, water is started through the mixing chamber and slurry pump, followed by the activation of the dry powder feed. Approximately 20 secs is required to blend the dry material into a slurry and deliver it through the slurry pump into the delivery hose.

Preformed foam was produced from commercial foam units using both protein and detergent-based concentrates. The essential elements of a foam unit are a tank for foam solution, a proportioner, and a refiner column. A 4 to 6% concentration of the foam concentrate in water is fed under pressure to the proportioner where it is mixed with air and fed to the foam refiner column. The proportioner may consist of either metering valves for both air and foam solution, or an orifice plate for the solution with a valve to regulate the air. The refiner consists usually of a 1 to 2 inch diameter copper column 1-1/2 to 2 feet in length, full of a suitable packing

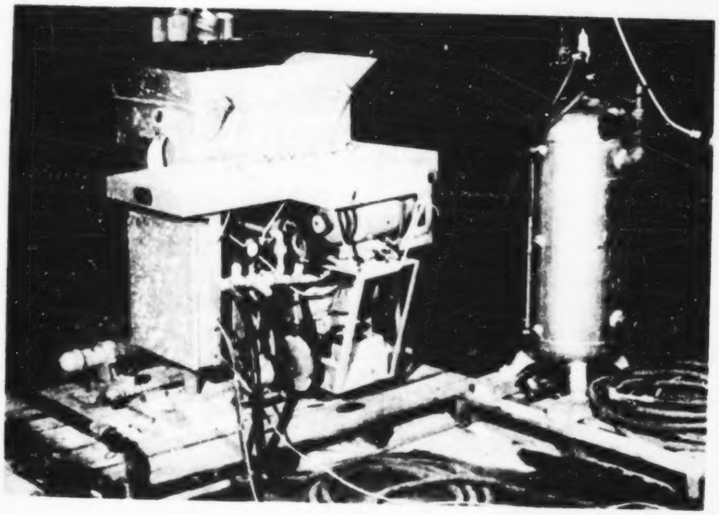


FIGURE 7 - MASON FLOW MIXER

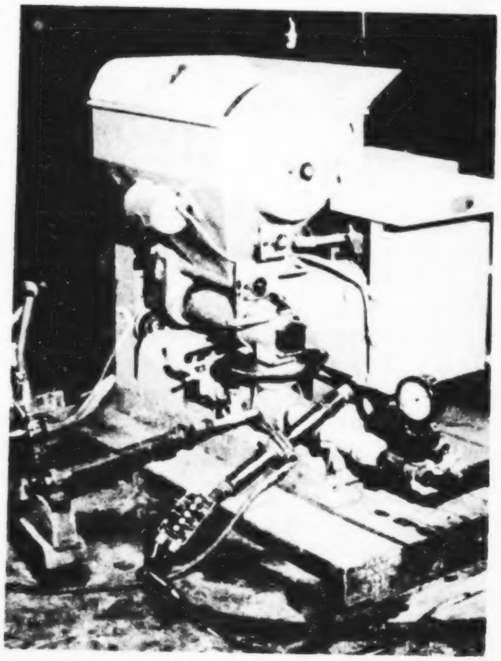


FIGURE 8 - FLOW MIXER SHOWING MOYNO PUMP AND DELIVERY SYSTEM

material (e.g., stainless steel wool, Raschig rings, Burrell saddles, etc.).

The proportion of air to dilute concentrate solution determines the foam density. The total pressure on the system (usually 45-90 psig) determines the rate of foam production.

Protein and detergent-based foam were each used initially in the studies. The protein foams were produced by Mearl Corporation -- Mearlcel for gypsum-based and Mearlcrete for cement-based mixtures. MSA's detergent-based foam concentrate was later found to be at least equivalent to the protein-based concentrates and compatible with both gypsum and concrete-based mixtures. Therefore, it was used almost exclusively in our test pourings and field trial studies.

A summary of our preliminary development runs is catalogued in Table 7. Some of this early work was conducted simultaneously with the laboratory studies and similar disappointing results were noted. They served, however, to confirm our laboratory results and to gain experience with the continuous mixer.

The initial unsupported barriers were produced with gypsum formulations (Runs 1-13). Set times of the order of minutes were achieved by adding accelerators, but the set was not fast enough to produce a non-flowing slurry.

Development work with commercial quick-set cement formulations was carried out with Huron Cement Company's Regulated Set Portland Cement (RSPC) (Runs 14-17). This is a special Portland cement supplied with an accelerator that produces an initial set in 5 to 15 minutes, depending primarily on water content and temperature. With added foam, the set time increased considerably and the cement was of poor strength and quality. The retarded set was likely due to the protein-based foam since some organics (e.g., proteins, sugars, starches, etc.) are known to retard the set of Portland cement.

The preliminary development studies on Halliburton-based formulations are summarized in Runs 18-32. The gypsum based formulations (Runs 18-21) set too slowly for our application. Following the lead of our laboratory studies, however, formulations containing sodium silicate as a fast gelling agent showed promise, and were slowly developed into barrier forming materials.

TABLE 7 - MASON FLOW MIXER TEST DATA

Run No.	Components	Set Time	Remarks
1	100 parts gypsum (molding plaster), 62 parts water	5 min	Low angle of repose, density - 112 pcf.
2	100 parts gypsum, 62 parts water, 13.5 parts Mearlcel foam 2 pcf	7 min	Low angle of repose, poor strength, density - 32 pcf.
3	71.5 parts gypsum, 62 parts water, 13.5 parts Mearlcel foam 2 pcf	16 min	Density - 32 pcf.
4	Slurry No. 1, - 100 parts gypsum, 62 parts water. Slurry No. 2, - 13.5 parts water foam containing 2.5% PVA, Borax added via Shot-Crete nozzle	--	PVA plugged the foam generator filter. Borax does not mix well through Shot-Crete nozzle.
5	100 parts gypsum, 62 parts water, 13.5 parts foam. Na_2SO_4 added with foam	--	Very poor foamed plaster - wet,soupy.
6	100 parts gypsum, 62 parts water, 13.5 parts foam, 0.1% Na_2SO_4 added with foam	--	No foamed structure produced.
7	Same as 6 except start gypsum before foam	--	No foaming action, plaster plugged in refiner and control valve.
8	100 parts gypsum, 62 parts water, 0.1% Na_2SO_4 with 16 parts foam added Shot-Crete nozzle	5 min	Low angle of repose, no flow after 2 minutes, density - 48 pcf.
9	Same as 8, increased foam and Na_2SO_4 content 50%	4 min	Too much foam, poor mixing, poor angle of repose.

TABLE 7 (continued)

Run No.	Components	Set Time	Remarks
10	100 parts gypsum, 62 parts water, 4.5 parts PVA, .08 parts Borax and 16 parts foam added to nozzle	3 min	Poor strength to foam structure, poor angle of repose, density - 35 pcf.
11	100 parts gypsum, 62 parts water, 4.9 parts PVA, .08 parts Borax and 16 parts foam added at nozzle	1.5 min	Low angle of repose.
12	110 parts gypsum, 62 parts water, 4.9 parts PVA, .08 parts Borax with 16 parts foam added at nozzle	5 min	Low angle of repose.
13	110 parts gypsum, 62 parts water, 4.9 parts PVA, .08 parts Congo Red with 16 parts foam added at nozzle	10 min	Low angle of repose.
14	Huron Reg-Set Cement, 2 turns on powder feed, foamed with protein-based preformed foam	no set	No set in 90 min, density - 33.6 pcf, low angle of repose.
15	100 parts Reg-Set Cement, 62 parts water, 13.5 parts foam with 4% silicate added at nozzle	20 min	Very friable structure.
16	100 parts Reg-Set Cement, 62 parts water, 5.5 parts dry bentonite, 13.5 parts foam in 20% Na_2SiO_3 protein added through Shot-Crete nozzle	25 min	Low angle of repose, poor strength, foamed mass, 42 pcf.
17	Same as 16 except foam and silicate added just after Moyno pump	45 min	Homogeneous foamed concrete of poor strength.
18	20 parts Portland cement, 80 parts flyash, 42.5 parts water, MSA salt-water foam (1.9 pcf)	no set	Poor foam-concrete, fly ash settled to bottom in 15 min.

TABLE 7 (continued)

Run No.	Components	Set Time	Remarks
19	20 parts Portland cement, 40 parts fly ash, 40 parts gypsum, 42.5 parts water. MSA salt-water foam (2.0 pcf) 5 gal/min	4 min	Very poor foam-slurry mixing. No strength after set.
20	20, 40, 40 parts respectively of Portland cement, fly ash, gypsum. 2.43 pcf foam blended in using in-line spiral mixer	--	Much more homogeneous foam cement, rather slow set and lacks strength, friable, density - 42.4 pcf.
21	Slurry No. 1, 20, 40, 40 parts respectively of Portland cement, fly ash and gypsum with 30 parts water. Slurry No. 2, 5.4, 30 and 64.5 parts bentonite, silicate and water	no set	Gelled, but too liquid. Low angle of repose. No set observed in 24 hrs, density - 45 pcf.
22	Slurry No. 1, 65.7 parts cement, 34.3 parts water. Slurry No. 2, 5.4, 30 and 64.5 parts bentonite, silicate and water. Ratio of Slurries 1:2 foam was 1:0.83:1	--	Low angle of repose. Gelled rapidly but lacked foam structure, density - 90 pcf.
23	Same as 22 increased foam delivery ratio	3-4 sec gel	Set in 9 min, low to medium angle of repose. Density of foamed cement varies from 93 lbs to 34.5 pcf.
24	Same as 22 and 23	3-4 sec gel	Poor foam blending. Set to a friable structure, will not support weight of a man. Density - 35 pcf.
25	Bentonite left out of formulation. Cement slurry of 66 parts cement, 34 parts water and foam (2.7 pcf). Silicate solution (50% grade 40* in water) added with water ring at shot-crete nozzle. Feed rates 87 lbs/min slurry, 10 lbs/min silicate solution	<15 sec gel	Very soupy formulation, low angle of repose. Density - 46.6 pcf.

TABLE 7 (continued)

Run No.	Components	Set Time	Remarks
26	Slurry of 67 parts cement, 33 parts water at 87 lbs/min, foam (3.3 pcf) and 50% silicate solution at 10 lbs/min	3-4 sec gel	Excellent angle of repose although inadequate foam content. Density - 68 pcf.
27	Same as 26	3-4 sec gel	Produced dike 8 in. high, 39 in. wide and 7 ft long. Density - 42.5, good foamed cement structure, medium angle of repose.
28	Same as 26 and 27 except silicate rate doubled. Slurry of 67 parts cement, 33 parts water at 87 lbs/min. Foam (1.5 pcf) at 15 gal/min and 50% silicate added at nozzle at 23 lbs/min	3-4 sec gel	Poor foamed cement consistency, rather soupy. Gel supported a 12 in. high dike, 24 in. wide. Friable cement, density - 71.6 pcf.
29	Same as 28 except more low density foam used. MSA Super Foam (3.2 pcf) at 16.5 gal/min	1-2 sec gel	Gel supported a 12 in. high dike. Excess displacement of first poured material occurs. Very strong cement.
30	Same as 29 except that MSA Super Foam introduced into Moyno pump along with cement slurry	1-2 sec gel	5 gal. MSA Super Foam in 17 and 30 seconds causes Moyno funnel to overflow. Output of Moyno pump too low for this method of foam introduction.
31	Same as 28 except MSA Super Foam (20 gal/min) introduced in slurry line immediately downstream of Moyno pump	1-2 sec gel	Highest degree of foam character in cement formulated to date. Gel supported a 12 in. high dike. Density of cement at beginning and end of pour 33 pcf. Very strong dike.
32	Same as 31 in all aspects	1-2 sec gel	Gel supported 15.5 in. high dike, 5 ft wide and 5 ft long. Base of dike slid as in 31. Foam cement density - 32 pcf.

*Note: Silicate used before dilution contains 37.1% $Na_2O \cdot 3.34\ SiO_2$

Because of the extremely fast gelling action of the sodium silicate, it was necessary to modify the generating and delivery system. The cement-bentonite slurries were formed in the Mason Flow Mixer and combined with preformed low expansion detergent foam downstream of the slurry pump. The silicate was subsequently blended into the foam slurry by the use of a shotcrete nozzle as it exited the delivery hose. A water ring, consisting of two circular rows of holes in the shotcrete nozzle, was used to inject the silicate solution.

In the initial formulations the development work stressed variations in the silicate concentration, bentonite addition, type and quantity of detergent foam formulation and technique. Quick gelling mixtures were obtained having densities of 32 to 93 pcf. In these runs two problems persisted: one was the tendency of the unsupported barrier base to be displaced by subsequent layers; and the second was the difficulty in obtaining a uniform foam delivery rate. Both of these problems are related; the first is a function of foam density and silicate concentration while the second is caused by variations in downstream slurry pressures. Air pressure was used to produce the foam, and to introduce it into the cement slurry mix. The rate of foam production and its addition is a function of the pressure drop across the metering system. Thus,as the viscosity of the cement slurry varied, the back pressure in the feeder line varied which affected the foam addition rate. This condition produced concrete of varying densities and support strength. In the first three runs (22-24), bentonite added to the slurry mix to increase its viscosity produced a high back pressure, resulting in foamed concrete in excess of 90 pcf. In Runs 25-32, therefore, the bentonite was not used. Although some improvement was noted, considerable density variations still persisted indicative of a foam feed-rate problem.

Although the presence of problems was recognized, it was apparent that the sodium silicate-gelled foamed cement offered promise for unsupported barrier formations. Accordingly, the remaining research and development effort centered on this formulation, and detailed data was gathered in an effort to delineate the conditions for best barrier production. This data and subsequent data for field test runs are summarized in Table 8.

The basic cement formulation for these studies contained 5% by weight bentonite. The slurry feed without bentonite was too thin to effect a reasonable barrier build-up. A concentration of 5% bentonite, however, materially aided in increasing the viscosity of the slurry without causing undue pumping problems. Starting in Run 59, additional lime was also added. Free lime is present in Portland cement. With

TABLE 8 - SUMMARY OF DEVELOPMENT STUDIES

Run No.	Mixer Feed/min.			Preformed Foam/min.			Silicate/min.		Total Water	Total w/c	Cement Silicate C/S	Run Time (min)	Dike Hts. (in)	Concrete Density (pcf)
	Cement(c) (lbs)	Water(w) (lbs)	w/c	Rate (gallons)	Density (pcf)	Water (lbs)	Neat Sol'n (lbs)	Total Water (lbs)						
33	58.2	29.1	0.50	15.2	3.2	6.1	11.6	16.2	51.4	0.88	5.02	6.7	24	35.1
34	54.4	29.1	0.53	15.0	2.8	6.1	11.7	16.2	51.4	0.88	4.65	5.5	16	34.8
35	55.2	29.1	0.53		2.4			21.3			3.61	2.8	16	35.0
36	55.2	29.1	0.53	15.6	2.2	3.9	15.3	21.3	54.2	0.92	4.21	6.1	17	37.0
37	58.2	29.1	0.50	13.6	2.5	4.9	15.6	21.5	55.5	0.95	3.73	6.0	20.5	34.0
38	58.2	29.1	0.50	15.6	2.1	3.7	15.1	20.8	53.6	0.92	3.85	6.2	20	34.0
39	58.2	29.1	0.50	15.6	2.1	5.8	16.1	22.2	57.1	0.98	3.61	5.8	19.5	32.0
40	58.2	29.1	0.50	13.9	2.0	3.5	15.2	21.2	53.8	0.92	3.83	7.5	26	34.0
41	52.5-43.2	29.0		13.9	4.1	5.6	12.5	20.3	54.9	varied		9.5	6	34.0
42	44.4	28.1	0.68	15.6	2.1	10.0	11.7	16.3	54.4	1.22	3.79	6.5	12	33.0
43	44.4	28.1	0.63	11.9	3.5	5.0	11.7	16.3	49.4	1.11	3.79	8.0	17	39.0
44	58.0	28.5	0.49											
45	52.5	28.5	0.49		2.0							4.5	16	35.0
46	52.5	28.2	0.54	14.3	2.4	6.2	15.1	21.0	55.4	1.05	3.48	9.1	21.5	37.0
47	52.5	28.2	0.54	16.7	2.1	6.2	12.1	8.0	42.4	0.81	4.34	6.0	15	28.3
48	52.5	28.2	0.54	16.7	2.2	9.1	4.7	3.1	40.4	0.77	11.22	5.0	6	29.0
49	52.5	28.2	0.54	18.2	2.7	7.8	4.6	6.3	42.3	0.81	11.54	6.0	6	36.0
50	52.5	28.2	0.54	19.2	2.8	6.8	12.3	17.2	51.2	0.98	4.27	9.0	19	33.0
51	56.5	28.4	0.50	16.1	2.7	7.0	8.8	12.2	47.0	0.83	6.42	9.0	15	38.0
52	56.5	28.4	0.50	16.1	1.8	6.0	11.3	15.7	50.1	0.88	5.00	7.5	16	36.0
53	56.5	28.4	0.50	11.9	2.7	4.6	8.3	11.6	44.6	0.79	6.81	7.3	17	38.0
54	46.0	28.4	0.62	15.0	3.0							3.0	4	41-52
55	47.0	28.4	0.60	15.6	3.7	17.4	16.6	23.2	69.0	1.47	2.83	5.0	16	36.0
56	47.0	28.4	0.60	15.6	3.1	11.8	16.2	22.6	62.8	1.33	2.90	5.75	18	36.0
57	47.0	28.4	0.60	21.2	3.6	11.5	17.1	23.9	63.8	1.35	2.75	9.2	25.5	40.0
58	47.0	28.4	0.60	20.8	4.2	13.7	15.6	21.8	63.9	1.35	3.01	7.8	19	38.0
59	47.0	28.4	0.60	14.3	2.5	4.65	16.9	23.6	56.65	1.20	2.78	5.0	16	41.0
60	47.0	28.4	0.60	28.6	2.0	7.34	10.9	15.2	50.9	1.08	4.31	3.75	8	22.6
61	47.0	28.4	0.60	20.0	8.1	8.02	10.9	15.2	51.62	1.10	4.31	1.0	-	32.0
62	52.0	28.2	0.60	20.0	4.8	12.8	16.7	23.2	64.25	1.23	3.11	4.2	12	31.4
63	52.0	28.2	0.54	10.0	2.2	3.01	12.5	17.4	48.7	0.94	4.16	7.6	16	47.0
64	52.0	28.2	0.54	14.3	2.8	5.2	23.4	32.6	66.0	1.27	2.22	5.0	8	51.0
65	52.0	28.2	0.54	13.6	2.4	4.2	16.4	22.4	54.8	1.05	3.17	5.5	18	39.2
66	52.0	28.2	0.54	13.0	3.1	5.4	13.9	19.4	53.1	1.02	3.74	5.7	18	38.8
67	52.0	28.2	0.54	12.0	3.5	5.4	17.5	24.4	58.1	1.12	2.97	5.0	(1)	35.0
68	52.0	28.2	0.54	12.0	2.1	3.4	15.6	21.7	53.3	1.02	3.33	7.5	13	34.6
69	52.0	28.2	0.54	18.8	Lost	-	Lost	-	-	-	-	4.0	8	27.5
70	52.0	28.2	0.54	13.0	5.2	9.0	16.5	23.0	60.2	1.16	3.15	4.6	3	34.6- 36.0
71	52.0	28.2	0.54	19.6	4.8	12.6	11.7	16.3	50.5	.97	4.44	8.5	13	47- 48.5
72	52.0	28.2	0.54	13.0	4.7	8.2	14.4	20.0	56.4	1.082	3.61	9.75	27	43.3
73	52.0	28.2	0.54	14.6	4.1	8.0	14.4	20.0	56.2	1.08	3.61	-	-	31.5
74	174.0	123.5	0.71	9.8	4.1	5.4	23.4	32.5	160.0	.92	7.4	2.5	13	55.5
75	101.0	71.5	0.71	19.4	4.5	11.2	18.7	26.1	109.0	1.08	5.4	4.9	13	31.1
76	121.0	85.5	0.71	43.8	4.5	25.3	40.8	57.0	167.8	1.39	2.97	4.0	14	35.0 42.0
77	91.0	56.9	0.625	26.0	4.5	15.1	33.8	47.0	119.0	1.31	2.7	4.5	14	32.0
78	68.0	42.3	0.625	38.1	2.5	12.2	29.5	41.1	95.6	1.41	2.3	9.5	14	29.0
79	77.0	38.0	0.50	22.0	4.0	11.9	19.0	26.5	64.0	0.83	4.0	11.6	14	37.0

our high sodium silicate addition, and resultant calcium silicate formation, however, we felt that the final cement blend would be deficient in lime. This additive proved to be beneficial and thus the cement mixture from Run 59 on consisted of 90 parts cement, 5 parts bentonite and 5 parts lime.

Our detailed study evaluated the water to cement (W/C) ratios of the slurry and final mix (adding in the water contributed by the foam and silicate solution) and the cement to silicate (C/S) ratio, as a function of dike height. Consistent dikes of over 16 inches were poured in Runs 33-40 with concrete densities of 32 to 37 pcf. A typical dike pour is shown in Figure 9. Gel structure breakdown, with a resultant slurry slide, limited the pour height to approximately 2 feet on a 12-16 inch wide base. Once the initial gel structure was broken, slides continued to occur along the same break line.

Short asbestos fibers (5% by weight) were introduced into the powder feed in Runs 41-43 in order to mitigate the slide problem. Back pressure surges, however, as determined from a pressure gauge in the delivery line, resulted in foam feed problems and a necessity for adding increased water. The total effect was to lower the dike height.

At the recommendation of Hoge-Warren-Zimmerman, the manufacturer of the Mason Flow Mixer, the preformed foam was added to the slurry in the Moyno pump chamber to overcome the varying feed rate of the foam generating unit. In order to carry the increased capacity of the slurry and the foam, it was necessary to increase the pumping speed of the Moyno, by a factor of four, to its maximum. Driving the Moyno pump at such high speeds caused troubles not previously encountered. Pumping the water-cement slurry and the preformed foam resulted in electrical overload and breaker cutout. In addition, it was very difficult to balance the flow of water-cement slurry and preformed foam delivery so as not to overflow the Moyno pump. Runs 44-59 summarize efforts to introduce the preformed foam and cement-water slurry simultaneously through the Moyno pump. These runs were very short lived; no sooner were flows established than the Moyno pump would overload and spill foamed concrete onto the floor.

Although homogeneous foamed concrete barriers of excellent height and strength were occasionally produced, the electrical overload problems made this procedure impractical. The slurry mixer automatically shut down several times during each run and was restarted only with difficulty to continue the run.

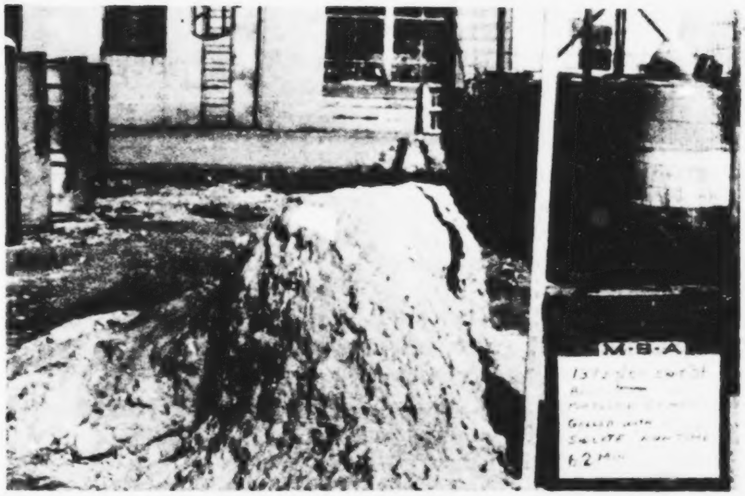


FIGURE 9 - FOAM CONCRETE TEST POUR SHOWING HEIGHT AND ANGLE OF REPOSE POSSIBLE WITH SILICATE SYSTEM

To avoid the Moyno feed and electrical overload problems, a pump was installed on the preformed foam unit to meter and pump the foam into the concrete downstream of the Moyno pump. This enabled us to reduce the speed of the Moyno and to add larger quantities of preformed foam consistently in order to produce lower density foamed concrete. At the same time a larger diameter delivery line was installed to alleviate high feed line pressures. The change enabled production of foam concrete as low as 23 pcf (Run 60). The resulting concrete structure lacked good integrity, however, which may have been due in part to a poorly blended foam slurry mix. Similar results were observed in Run 61. This method of foam introduction greatly improved the operation in that it eliminated the electrical overload problem.

The one inch (I.D.) spiral mixer-delivery hose system was installed in the above system to provide additional blending action of foam and slurry. This action produced reliable barriers of significant height (Runs 62, 63, 65). Run 64 had a malfunction in the silicate feed system.

As mentioned previously, Run 59 presents the data for a formulation consisting of 90 parts cement, 5 parts bentonite and 5 parts lime slurried and gelled with silicate to produce a 16 inch high, 9 inch wide and 6 foot long barrier with the qualities of block wall. This was a most successfully prepared barrier, emboding all the requirements of the program -- quick gel in 2-3 seconds, high angle of repose, no displacement during pour and exceptional strength 1-1/2 hrs after placement.

Field Tests

Field tests were conducted with the Mason Flow Mixer on the ability of the quick-set foamed concrete formulation to block and impound flowing liquids. The powder feed for the tests consisted of:

	Parts by Weight
Cement	90
Bentonite	5
Lime	5

The unit was placed on a flat bed truck for the tests and connected to water, air and power supplies at the test site. A mobile compressor provided the necessary air.

A problem with the unit, as far as its utility in an emergency system, was found during these tests. In order for proper water mixing to occur, the unit must be nearly level. A slight slant rearward allows the water to flow backwards out of the mixing chamber without contacting the powder feed.

The powder, water and silicate feed rates were held constant throughout the runs, and as closely as possible to conditions for Runs 62-65, which gave reasonable dike heights. Some problems were encountered during sub-freezing weather, causing changes primarily in foam feeds. The run data are summarized as Runs 66-73 in Table 8.

In the initial test (Run 66), a concrete barrier 16 to 18 inches high and 8 feet long was erected across a depression at the same time as water flowed into the impounded area at a rate of about 12 gal./min. The foamed concrete was excellent (39 pcf) and gave no evidence of disintegration even though the gel set alone was providing the barrier strength. Very small leaks appeared under the barrier approximately one hour after water flow started but days later had not enlarged. The pictorial progress of the test is shown in Figure 10.

In Runs 67-68 water flow was started through a depression at a rate of about 17 gal./min before the dike formation was attempted. Run 67 was unsuccessful. The water flow immediately washed away the freshly poured foamed concrete. To overcome this situation, the flowing water was allowed to leak through a gap on a section left open in the foam concrete barrier. The barrier was erected from both sides of the depression to the gap and allowed 2 minutes set time. A piece of sheet metal was then inserted as a sluice gate in the gap to stop the flow. Immediately upon application of the sluice gate, foamed concrete was poured behind it to strengthen and tie together the two barrier sections. In approximately 4 minutes the reservoir filled to a depth of about 10 inches and at that same time the barrier around the sluice gate failed.

In Run 68 a barrier was successfully built across a water flow of 15 gal./min in 7.5 minutes. The barrier averaged 10 to 13 inches in height, 9 inches thick and 9 feet wide. The impoundment was full (10 inches deep) in 22.5 minutes.

The difference between Run 67 and 68 in the ability of the barrier to stop flowing water is apparently a function of the hydraulic head build up rate on the barrier. Run 68 filled to a depth of 10 inches in 22.5 minutes, whereas Run 67, which failed, had a smaller impoundment area, and filled to a similar depth in only 4 minutes. The slower fill rate obviously allowed additional strength to develop in the dike material.

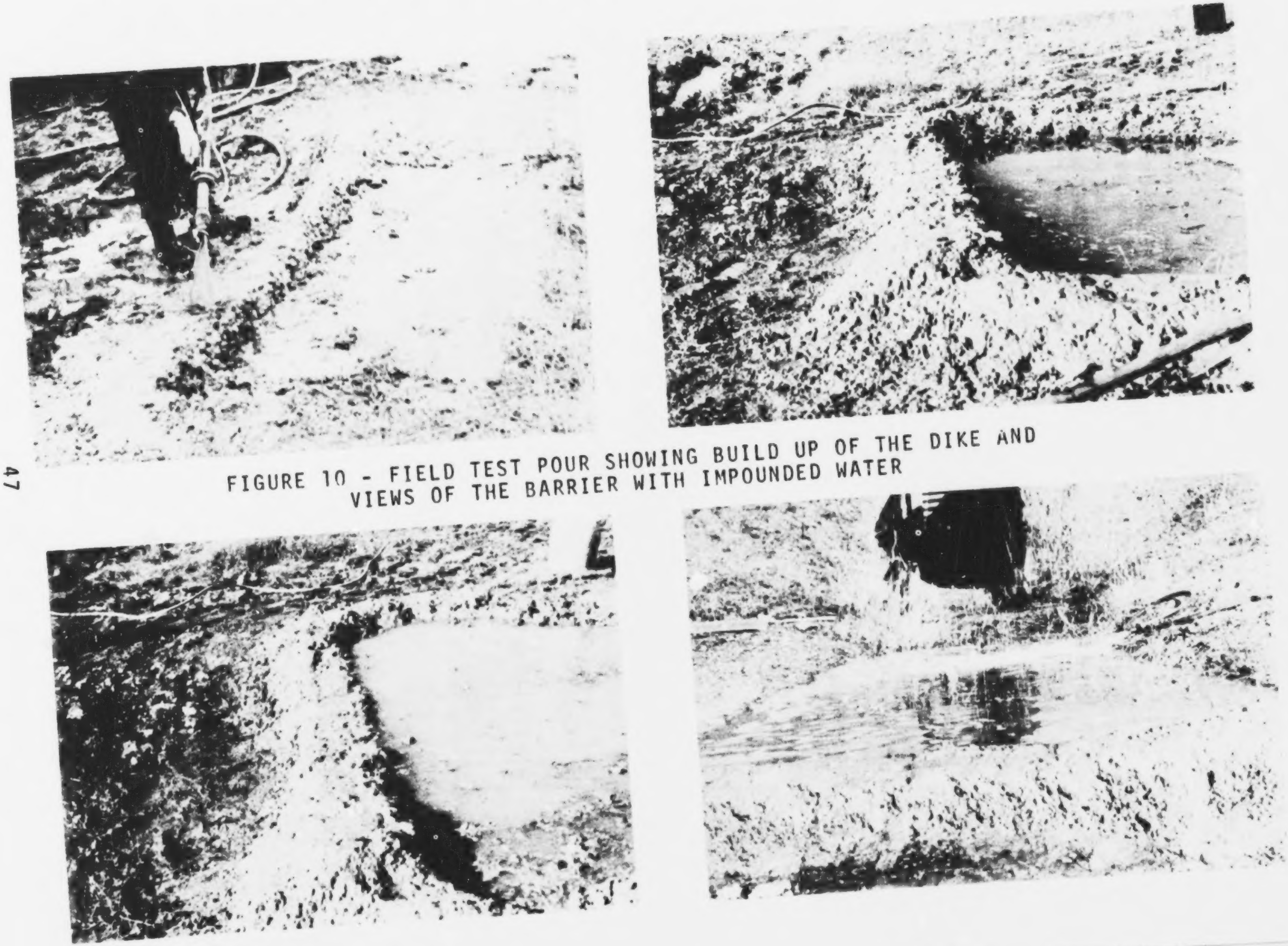


FIGURE 10 - FIELD TEST POUR SHOWING BUILD UP OF THE DIKE AND VIEWS OF THE BARRIER WITH IMPOUNDED WATER

At ambient temperatures below 32°F, further field test work was adversely affected. At these temperatures, the foam solution lines and various water lines on the slurry mixer tended to freeze (Runs 69, 70). The incorporation of either aliphatic or polyhydric alcohols in the foam solution alleviated the freezing problem but unfortunately these antifreeze materials retarded the cement set and the foam concrete tended to be easily dissociated by flowing water.

The use of inorganic solutes, $CaCl_2$ and NaCl, in high concentration to lower the freezing point of the detergent foam solution resulted in poor concrete quality ($CaCl_2$) or poor foam quality (NaCl). A barrier to a 15 gal./min flow of water using MSA salt water foam and 5% $CaCl_2$ solution produced a 13 inch high barrier of 47 to 48.5 pcf concrete (Run 71). The concrete was of poor integrity, slow to gel and tended to dissociate.

Run 72 was conducted on an above-freezing day without added anti-freeze material in the foam, to test our feed rates on the equipment. The barrier height of 27 inches was one of the best dikes produced.

Run 73 was run in sub-freezing weather using sodium hydroxide to lower the freezing point and Derifat 160-C, a foam agent from General Mills, Inc. The foam cement tended to gel rapidly but was lacking in strength.

The field tests using the Mason Flow Mixer established the utility of foamed concrete as a barrier for hazardous material spills and the feasibility of erecting barriers under field conditions. The two problems encountered, however, orientation sensitivity and cold weather dike formation, need further investigation.

Following the field tests discussed above, an MSA Model 2000 slurry rock dust distributor was evaluated as an example of a batch operation foam concrete generator. The unit, shown being used for making a typical barrier installation in Figure 11, consists of a slurry tank of approximately 200 gallons capacity, and a Moyno pump for slurry delivery. Both the Moyno and the slurry tank agitators are powered with variable speed hydraulic motors, which are in turn powered by an electrically driven hydraulic pump. A pump was employed to introduce the detergent foam downstream of the Moyno pump. The hose delivery system and silicate blending nozzle used on the Mason Flow Mixer were also employed on this system.

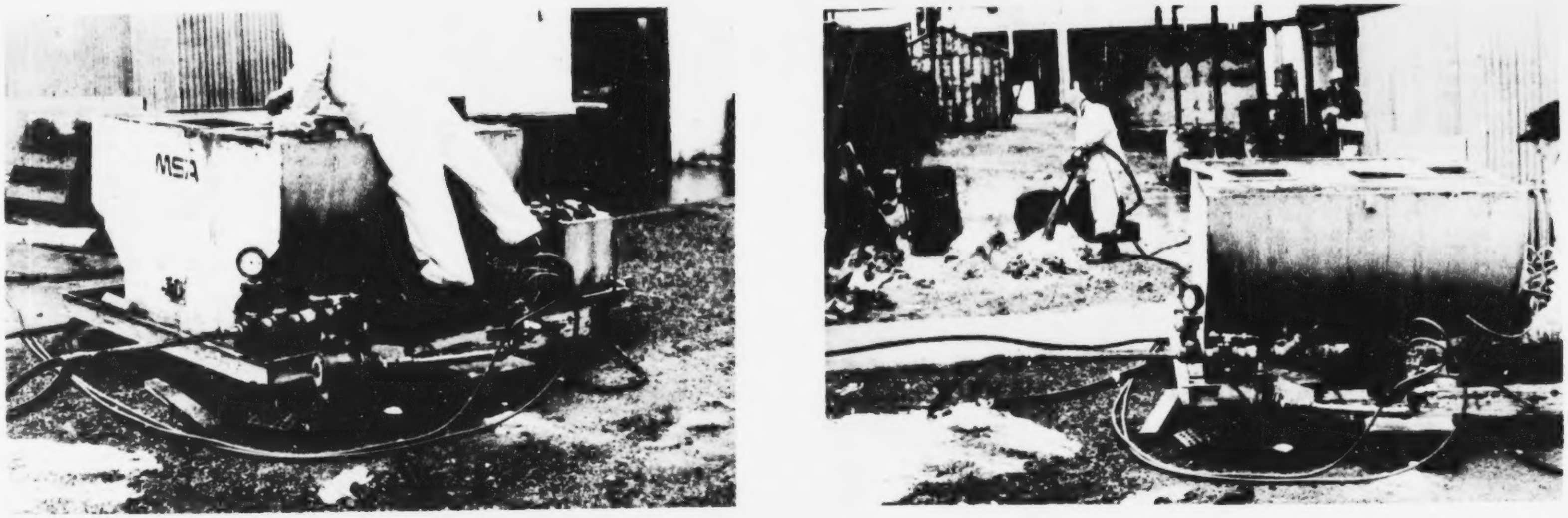
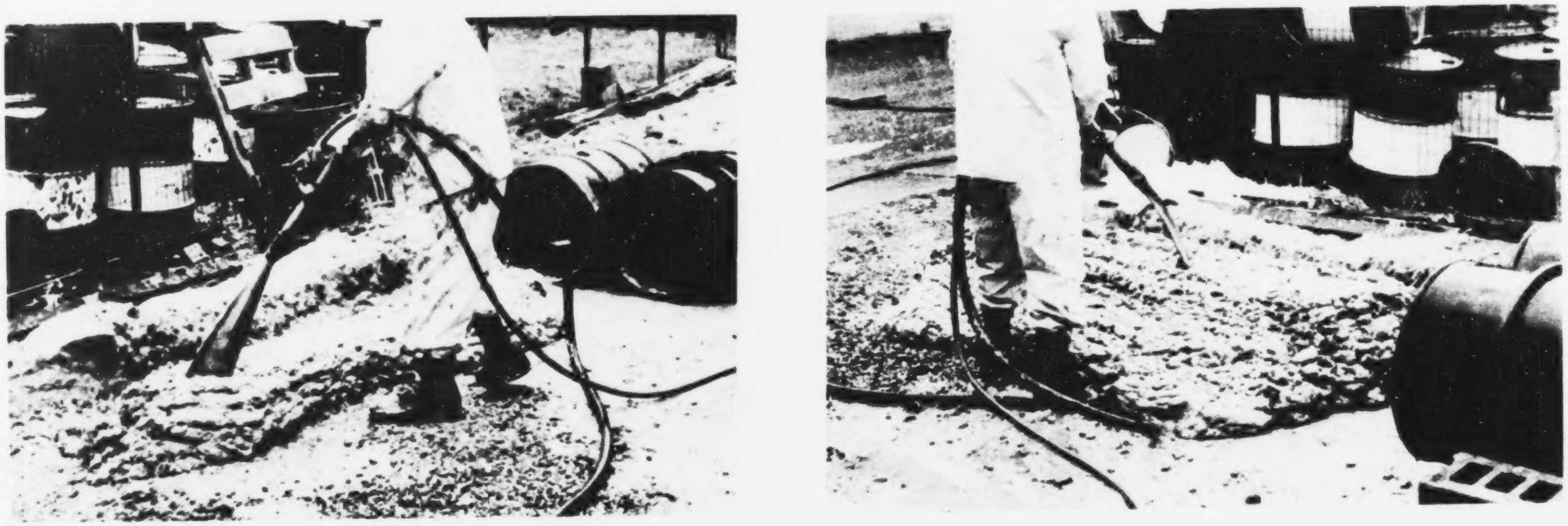


FIGURE 11 - POUR OF FOAM CONCRETE USING MSA BATCH TYPE MIXER



The advantages of using a batch system, rather than the continuous unit like the Mason Flow Mixer, are simplicity and ease of field operation. A batch unit eliminates the need for metering the powdered solids and water feed. This unit also would operate in off-level positions.

The data for the runs with the slurry rock duster are summarized as Runs 74-79 in Table 8. Improved weather conditions during this test period permitted the use of the detergent foam without added anti-freeze.

The ability of the foamed concrete to form barriers throughout the six experiments was generally inferior to that finally developed from the continuous mixer. Problems were experienced initially with extremely rapid slurry feeds and balancing the preformed foam and silicate solution feeds to the slurry. In order to obtain good powder mixing within the slurry tank with the small agitators normally used to slurry the rock dust, an abnormal amount of water had to be employed. Whether due to this or to unbalanced preformed foam or silicate feeds, barrier heights exceeding 14 inches were never realized. Poor gel formation, resulting in slides, inevitably held batch processed dikes to the above height limit.

Only in the last run (Run 79), when the water to cement ratio was held at 0.50 in the slurry tank with additional stirring to allow for mixing, did we obtain foam concrete of quality similar to that obtained from the Mason Flow Mixer. However, we could not form more than a 14 inch barrier before running short of foam concrete. Additional material was available in the hopper, but at the lower water to cement ratio it was difficult to achieve flow from the hopper into the Moyno pump at a rate sufficient to stabilize the feed of preformed foam and silicate.

Summary

The feasibility of foamed concrete to produce a dike which will hold back or impound a typical spill of liquid has been demonstrated. Tests on such varied substrates as clay, shale, chipped limestone, grass and weed-covered ground have been successful. Screening tests have shown that such hazardous liquids as methanol, 1,1,1,trichloroethane, phenol, acetone cyanhydrin and acrylonitrile do not affect freshly poured foam concrete.

The rate of build up of hydraulic head on the barrier system is probably the single most important factor to successfully impounding a spill. An extremely high liquid velocity would probably not allow barrier formation in the flowing stream. In such a spill, however, most of the contents would likely be lost and the damage done before emergency equipment could be brought to bear. Where low flow velocities are present, or a large impoundment area available to allow filling over a period of 15 minutes or more, a foam concrete dike could be successfully employed.

Although our experience with the batch type mixers was limited, we believe that the batch type operation offers the most simple approach to an emergency field unit. A possible design for such a unit is shown in Figure 12. The unit is trailer mounted, suitable for a pick-up truck operation. It would produce approximately 50 ft^3 of foamed concrete at 45 pcf per batch within 30 minutes of delivery to the site. Repeat cycles would take approximately 25 minutes each.

Three such batches (150 ft^3) could be produced in approximately 80 minutes to build barriers of such sample dimensions as:

2 ft x 2 ft x 38 ft

1.5 ft x 2 ft x 50 ft

1.5 ft x 3 ft x 33 ft

Raw materials for one batch are:

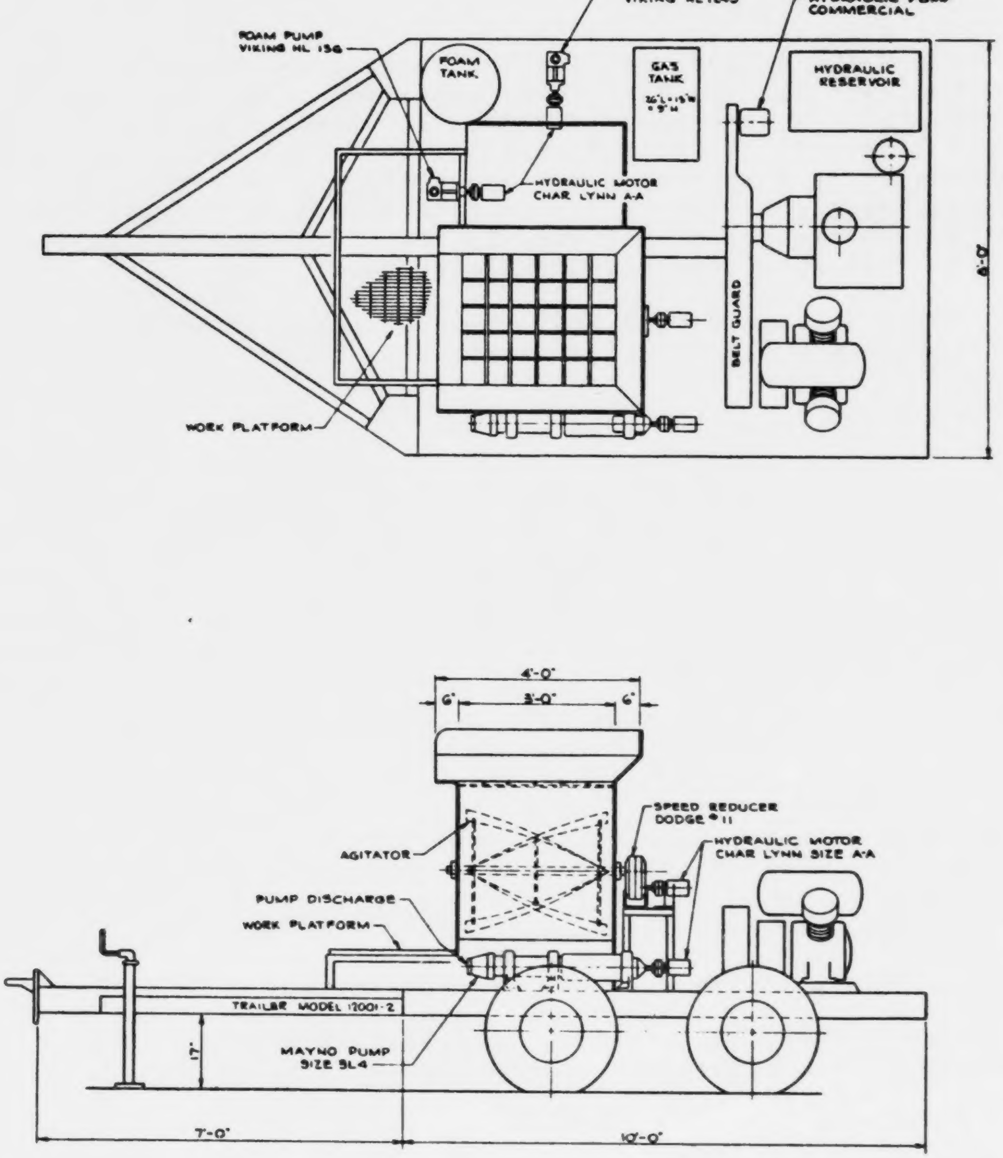
10 bags of cement (940 lbs)

30 gallons of sodium-silicate solution

1.5 quarts of foam concentrate

Material for one run would be transported on the unit. Material for three batches would weigh approximately 4900 lbs and require about 1800 lbs of water (215 gal.) at the site. Additional material could be brought in if needed.

The sodium silicate and foam concentrate would be the only material required to be stored in quantity for multiple batches. Enough Type I cement could be stored for 1 to 3 batches, with additional cement picked up as needed.


SILICATE PUMP
VIKING HL 124S
HYDRAULIC PUMP
COMMERCIAL
FOAM PUMP
VIKING HL 136
FOAM TANK
GAS TANK
26"L × 15"W × 9"H
HYDRAULIC RESERVOIR
HYDRAULIC MOTOR
CHAR LYNN A-A
BELT GUARD
WORK PLATFORM
6'-0"
4'-0"
6"
3'-0"
6"
SPEED REDUCER
DODGE # 11
HYDRAULIC MOTOR
CHAR LYNN SIZE A-A
AGITATOR
PUMP DISCHARGE
WORK PLATFORM
TRAILER MODEL 12001-2
17"
MAYNO PUMP
SIZE SL4
7'-0"
10'-0"

Scale: 3/4" = 1'0"

FIGURE 12 - PROPOSED EMERGENCY FIELD UNIT

SECTION VI

HIGH EXPANSION SYSTEMS

In the majority of spill situations the demand for control materials will exceed the supply. An alternative to providing larger portable or mobile units is to increase the expansion ratio of the original starting material. The commercially available foam formulations of urethane and foamed concrete available at the beginning of the EPA program offered an expansion of only up to 35:1. It was of interest to examine the use of material which would offer at least 3 to 4 times these expansion ratios. This phase of the report deals with the screening,selection and evaluation of highly expanded materials capable of serving as a suitable hazardous material land spill barrier. Some of the work performed in this phase served as a basis for the higher expansion urethane reported in the previous phase.

The search for candidate starting materials focused on materials which were polymeric in nature or capable of being polymerized or gelled to a highly expandable, rigid chemically inert foam structure. There were two candidate materials -- water soluble polymers and conventional rigid foam systems. The water based systems were capable of high expansion but needed development in rigidizing. The rigid foams had not been developed for high expansion.

The primary requisite for each candidate system was that it be amenable to foaming. Methods of generating a foam varied considerably due to the peculiar physical and chemical properties of the test solutions. For the most part, conventional foam generating hardware was used and modified as required.

Water Soluble Systems

Polyvinyl Alcohol - Borax Gel

Primary emphasis in the water soluble polymers focused on solutions of polyvinyl alcohol since such systems can be solidified after foaming. In general, different grades of PVA exist and the properties are dependent upon the molecular weight and the degree of hydrolysis. Maximum film strength and solvent resistance are generally obtained from the high molecular weight, highly hydrolyzed grades. All grades of PVA are water soluble but the types of interest were generally only soluble in boiling water. Prepared PVA solutions of 5% and greater are extremely viscous and not amenable to conventional foaming.

A 1% solution of PVA can be readily foamed, especially with the aid of a surfactant. The foams produced possess no outstanding properties although the mass of foam may have a somewhat longer life than normal surfactant foam. The interaction of borax with PVA is rather striking. For example, as little as 0.1% of borox in a solution of 5% PVA causes immediate gellation. Physically, the entire solution forms a firm, solid mass.

All attempts to produce a high expansion foam from solutions of PVA and borax were unsuccessful. The major difficulty with this system was the rapid rate at which gellation occurred. Instant gelling occurred in the solution if there was any delay time in foaming the solutions after they were mixed. Similarly, any solution holdup, runoff or drainage almost immediately formed a firm immovable mass which caused plugging or fouling in the generating hardware.

It was obvious that this system posed serious mechanical problems. Admittedly, it may have been possible to generate foam using a more highly developed mixing chamber. However, an examination of the PVA-borax gel prepared without foaming indicated a texture that was firm but somewhat brittle. Ideally, materials best suited for foam are somewhat free flowing and elastic. These properties are generally important in preserving structural integrity of the foam while the excess water drains or evaporates. In view of these mechanical and physical weaknesses it was considered that the PVA-borax system was a poor choice for further development.

PVA-Congo Red Gels

Solutions of PVA can also be gelled by the addition of Congo red. This system forms a thermally reversible gel in that below 40-45°C the solution is solid and above which it is liquid. The warm liquid solution foams exceptionally well with or without the addition of a foaming agent or surfactant. The properties of the PVA-Congo red gel were found to be more consistent with the needs of this program. In general, the gels were extremely adhesive, tough and elastic. Foam masses dried to an extremely tough durable cover which adhered well to smooth surfaces such as glass and metal.

Solutions for foaming were prepared as 5 wt % solutions of PVA in water (duPont Elvanol 72-60). In preparation to foaming, the solution was raised to 70-80°C and Congo red added at 0.3-0.4 wt %. In some cases a liquid surfactant was added. The surfactants were generally maintained at about 1-3 wt % in the final solution. Generating low expansion foam from a 40-50°C solution could be accomplished by a number of methods. However, the foams blown could not be considered for diking systems. In general, foams blown from solution at 45°C were of low expansion requiring about

5-10 minutes to develop a reasonably non-flowing structure but some several hours to develop a strong matrix. The dried masses were surprisingly strong and resistant to water and other chemicals, such as acetone.

The results of preliminary tests were encouraging but the time required to develop strength along with the need for a warm solution were recognized as major weaknesses. In addition, preliminary results were obtained at a relatively low expansion of 30:1. Studies were conducted to circumvent the need for elevated temperatures and to examine the foam quality produced at higher expansion. Hopefully, eliminating the temperature requirement would also benefit the set time.

Several attempts were made to blend the two separate solutions together immediately before foaming. In these tests the ingredients were at room temperature. Aqueous solutions of PVA at 6% and Congo red at 0.4% were charged in separate pressure tanks. Each tank was pressurized to 100 lb with nitrogen. Needle valves at the exit end metered the flow from each tank. The output of both tanks were blended together immediately before entering the high expansion properties system. Results of these runs showed the PVA Congo red foams without added surfactant could not be foamed. With an added foam agent, a high expansion foam (150:1 expansion) was formed which possessed poor structural strength and no apparent life or stability.

PVA-Metal Ion Gels

Other reagents reportedly able to gel PVA were also examined.[8] These included chromium (III) and titanium (IV). Chromium (III) was generated in the final mix by incorporating sodium chromate in a slightly acid solution in one tank and a 6% PVA solution containing a small amount of sodium sulfite in the second tank. The intent was to combine the acid and sulfite together and reduce the chromium (VI) to chromium (III). The chromium (III) was then to gel the PVA. In a similar manner attempts were made to gel the PVA by the use of titanium (IV) added in the form of potassium titanium oxalate. The results were similar to those obtained with Congo red. Foams could not be produced using the high expansion system without the presence of a foaming agent. Even with a foaming agent the freshly generated foam failed to develop any structural strength. At expansions greater than 150:1, which could only be achieved with the use of added foaming agents, the life of the foam was exceptionally short. There was no true gelling and generally total collapse occurred within one hour.

It appeared that the PVA-gellant systems were not amenable to conventional high expansion generation methods. Another mode of operation was explored. The two streams consisting of 6% PVA and 0.4% Congo red were metered together at a cross. The blended streams were simultaneously mixed with a flow of nitrogen and the combined output was fed to a one foot by one inch diameter chamber of metal helices.

The foam produced by this system was of low expansion (∿30:1) but with improved life. However, the foam was a free-flowing mass with no structural strength.

Miscellaneous PVA Studies

In additional efforts with PVA systems, several attempts were made to minimize the use of some of the water by dispersing the Congo red in a mixture of methylene chloride and Freon 12. The intent was to use the Freon as a blowing agent. The PVA and the anhydrous Congo red solution were mixed and foamed into a warm tray to volatilize the Freon. Foams produced in this manner were of low expansion (30:1) and in all but one case were relatively quick to shrink and/or collapse. In one singular case a stable structure was formed which when thoroughly dried was exceptionally tough and durable. The matrix of this material consisted of bubble sizes averaging 1/4 inch diameter. This was not reproduced in subsequent tests. It was strongly suspected that this gel was similar to the thermally reversible gel discussed earlier.

In addition to the above approach, numerous support materials were added to the Congo red-PVA system in an attempt to build immediate strength into the foamed mass. Table 9 lists the additives tried but all such attempts failed.

Emphasis shifted to other water soluble polymer systems, particularly those which could be employed at higher initial concentrations. Of special interest were the Acrysols of Rohm and Haas. This class of materials is acidic and when neutralized forms soft gels at concentrations of 1-2% of the neutralized polymer. The Acrysols are supplied at ∿28% concentration in water. ASE60 was used as representative of the Acrysols.

Neutralization and subsequent gellation can be induced by the addition of a number of basic materials including sodium and ammonium hydroxide, amines, etc. Neutralization by sodium carbonate was of special interest since carbon dioxide would be liberated to enhance the foaming action.

TABLE 9 - EFFECTS OF ADDED POLYMERS ON PVA-CONGO RED SOLUTIONS

Base Material	96 ml of Additive	Remarks
240 cc of 5% PVA(1) 66 cc of 3% Congo Red(2)		
	Water	Gels fast, develops a strong elastic foam.
	0.5% Poly M-295	Good foam, relatively stable (~16 hr), weak structure.
	PCS Glue,2%	Foams well but unstable.
	Stymer S, 5%	Gells immediately, no foam.
	Methyl Cellulose,2%	Forms a gel with Congo red. Foamed mass weaker than PVA-Congo red.
	Acrysol GS, 3%	Good foam but unstable.
	Low molecular weight PVA, 5%	Poor foam, weak structure.
	Methocel MC, 2%	Gels with Congo red alone. Inferior to PVA system.
240 cc of 5% PVA(1) 50 cc of 4% Congo Red		
	Amisol, 3%	Slow to set, excellent foam quality after 16 hr.
	Gelgard	Similar to PVA Congo red alone
	PVP-K-30, 10% (Polyvinylpyrrolidone)	Unstable foam
	Amisol, 12%	Good foam, extremely tacky,>4 hr stability, weak structure
	Carbopol 941, 0.5%	Unstable foam

(1) Elvanol 72-60 (duPont)

(2) Congo red dispersed in water

A number of runs were made in which ammonia vapor and vapors of various amines such as triethylamine and diethylenetriamine were metered into the air stream. The results were not fruitful. When the amine or ammonia was used in lesser amounts, the generated foam was no better structurally than the ASE60 used alone. At higher stoichiometric amounts of the basic vapors, gellation occurred in the generator causing immediate clogging.

Use of inorganic type base such as sodium hydroxide and sodium carbonate produced a somewhat less elastic type foam. With the addition of sodium carbonate, the liberated CO_2 caused foaming of the gelled solution but in all cases the generated foam possessed a wet strength no greater than shaving cream.

When it was apparent that none of the systems investigated showed promise for the further development of a foamed mass with sufficient wet strength to serve as a spill barrier or diverter, this phase of the program was terminated. This was prompted additionally by the fact that a parallel program conducted intermittently with the studies described above but focusing on a conventional rigid foam formulation was showing considerable promise.

Conventional Rigid Foams

The most simplified polymeric system from an application point of view is undoubtedly the rigid urethanes. The nominal working density of conventional polyurethane is about 2 pcf although densities of the blown foam can approach that of soft pine or about 22 pcf. Although there have been reports of urethane as low as 1 pcf, which offers an expansion of about 75:1, there was little if any information of lightweight material in the 0.25-0.50 pcf range.

An alternative to the urethane is the urea-formaldehyde type formulations. Several contacts with industrial applicators of this type system indicated that this finished foam would not retain sufficient structural strength. A sample of a urea-formaldehyde foam at approximately 0.6-0.8 pcf was received and was found to be exceptionally weak. In fact, the material hardly survived shipment to the laboratory. A concerted effort was therefore directed toward the development of a urethane type formulation with the basic urethane properties but a density of less than 1 pcf. This work was initiated in parallel with that of the first phase on this program. Formulation investigations to yield urethanes less than 1 pcf were performed in this phase along with preliminary tests. When it became clear that densities less than 0.5

to 0.6 were not practical, further development and testing of the higher densities were transferred to the first phase.

Low Density Urethane

The chemistry of urethane foam is complex. In brief, the essential ingredients of a urethane formulation consist of a polyol, polyisocyanate, a surfactant, catalyst and blowing agent. In operation, the polyol and the isocyanate in the presence of a suitable catalyst react to form the plastic polyurethane. The reaction is accompanied by the evolution of considerable heat which tends to boil the added blowing agent,in turn causing the plastic mass to foam. The surfactant or cell control agent regulates the foaming phase so that uniform cell structures are obtained. Although these are the necessary ingredients of the foam, numerous combinations of ingredients are possible due to the availability of a selection of polyols, catalysts and blowing agents. As stated earlier, blowing agents most commonly used are the Freons; however, any low boiling component could be considered. Water is not only a reactant (polyol) but can also serve as a blowing agent since the reaction of the isocyanate with water yields carbon dioxide.

Laboratory development studies were performed to assess the effects of varying the essential ingredients. In practice, all ingredients except the isocyanate were first added and mixed with a stirrer. The isocyanate was injected into the stirred solution using the calibrated barrel and plunger of a syringe. A representative type formulation for a 2 pcf density urethane foam is shown below:

Activator	Parts by Weight
Isocyanate - Mondure MR (Mobay)	138
Resin Mix	
Polyol - Poly G435 (Olin)	129
Blowing Agent - Fluorocarbon II	40
Catalyst DABCO 80-20 (Hoodry)	1
Surfactant DC 193 (Dow Corning)	1

Familiarizing runs were made using a base formulation and merely incorporating more blowing agent into the mix. The excess blowing agent did produce a somewhat higher expanded foam but the foam was of poor quality as evidenced by the relatively large and uneven cell sizes. Eventually, with increasing amounts of blowing agent, additional amounts of catalyst were required to initiate the reactions. Foam densities ranging from 0.8 to 1.0 pcf could be obtained by this approach; however, the solution now was unwieldy with the excess blowing agent and catalyst.

Water was next added to the mix with triethylamine (TEA) found to be the most effective catalyst. Numerous attempts then followed to obtain the proper combination of polyol-water and the required amount of TEA catalyst. The work was performed by maintaining a master mix of the polyol, surfactant and fluorocarbon in one solution and varying the amount of water and/or catalyst. Excellent foam textures could be produced in the range of 0.6 to 0.7 pcf. However, all foam was found to shrink upon standing. Shrinkage was attributed to the pressure differential formed in the individual cells when the gas phase cooled. The degree of shrinkage was sufficiently serious to indicate the likelihood that the applied foam would tear itself away from the surfaces upon which it was deposited. Ultimately, it was found that non-shrinking foams could be formed by using methylene chloride in place of the fluorocarbon. With some modification in the polyols and the amount of TEA catalyst, it was possible to form a high quality foam in the range of 0.6 pcf (expansion ratio 115:1).

A secondary development of the study occurred when it was found that water with TEA could react with the isocyanate to yield a foam-like material By optimizing the amount of TEA catalyst it was found that high quality foam down to 0.29 pcf could be routinely made in the laboratory. Visually, there were no apparent differences in the water/TEA/isocyanate foam generated at 0.3 and 0.6 pcf when compared to material with the conventional 2 pcf density. The lightweight material was, of course, weaker but considerably less brittle than the high weight material.

Evaluation Tests

The screening studies had been unsuccessful in defining a useful water soluble polymer system, but the urethane type materials were sufficiently encouraging to move candidate systems on to further evaluation. The failure of the water soluble polymer approach to yield a promising candidate was attributed to the use of excess water associated with these systems. Realistically, the foam masses which were formed consisted of 95-97% water. In general, the excess water provided the necessary flexibility in the generated foam to allow for shrinkage during the subsequent drainage or evaporation stages. At the same time the presence of available water inhibited the formation of the required rigidized structure. Maximum strength would not be achieved until the foam masses approached dryness and this required several hours at best. The only systems which might circumvent the difficulties involved either increased temperature and/or the handling of highly dangerous peroxide type chemicals.

The results obtained with the low density urethane-type foams were quite encouraging. The expansion with the lightweight material (230:1) was undoubtedly much greater than could possibly have been achieved with a practical water soluble polymer system.

The evolved formulations were of particular interest for another reason. Both formulations (0.6 pcf, 0.29 pcf) utilized water. It was now possible, if required, to incorporate into the urethane mix the water soluble polymers which by themselves were found ineffective. In this respect the water-isocyanate reactions were the quick set mechanisms lacking in the water soluble polymer systems. At this point the possibilities for a high expansion polymer system appeared very promising.

Preliminary spray tests using conventional urethane spraying systems were conducted on both formulations. The results of these tests are described separately.

Water-Isocyanate Mix (0.3 pcf)

The extremely low density formulation consisted of the following:

Activator	Parts by Weight
Mondure MR (Mobay)	10
DC 195	∿0.25
Resin	
Water	2
Triethylamine (TEA)	2

The two reagent solutions were stirred thoroughly immediately before charging to two separate pressure pots. Each pot containing the mix was pressurized to 100 lb with nitrogen. Throttling valves at the end of each tank metered the flow from each side. Both streams were fed to a conventional Binks 18 FM Mine Gun which is standard urethane hardware. Spray tests were conducted indoors at about 70°F. Optimum foam generation using this system consisted of 3.5 parts activator to 1 part water-catalyst mix.

The foam mix was sprayed onto both smooth cardboard and concrete. The freshly sprayed material appeared as a free-flowing liquid and tended to run off vertical surfaces. Cream time or the time for initiation of rise was approximately 3 seconds. After the initial period, the rise of the applied foam was remarkably fast. Time to achieve full rise was about 5-7 seconds.

It was found that the applied foam did not adhere well to either the cardboard or concrete surfaces. In addition, considerable amounts of vapors of TEA were evolved during the actual spraying and subsequent reaction. Sections of the applied foam showed a density of 0.35 pcf which approached the laboratory data.

It had been suspected that in the formation of a lightweight foam much of the cell structure would remain open. It was of interest to determine the resistance of the specialized foam to penetration by liquids.

Sections of the sprayed foam were immersed under 8 inches of water containing a dissolved dye (Congo red) and a wetting agent (Aerosol OT). Time of immersion was about 16 hours. By visually examining sections of the test foam it was found that depth of dyed liquid penetration was generally about 1/8 inch into the foam interior. Some sections of the test specimens showed deeper penetration but these occurred at the interface between two distinct layers of foam. Thus, to build up a layer of foam 4 inches or more, it was necessary to apply the spray in at least two passes allowing the first coat to expand fully. Maximum dye penetration was observed along the surface between the two layers.

These tests of foam generated with conventional hardware showed the major weakness to be the lack of adhesion to smooth surfaces. In all other respects the generated foam was structurally sound.

Methylene Chloride Mix (0.6 pcf)

The formulation for a 0.6 pcf foam consisted of the following:

Activator	Parts by Weight
Mondure MR	1.3-1.4 per 1.0 of resin mix

Resin	Parts by Weight
Polyols G460	24
UI800	3.5
Surfactant DC 195	1
Methylene Chloride	8.2
Water	11.4
DMEA	11.4

Spray tests were conducted similar to those described with the lighter material. Optimum foam production was achieved at a ratio of 1.3-1.4 activator to 1 of resin mix. Fumes of DMEA were minimal.

The sprayed solution was free flowing with a cream time of about 4 seconds and reaching a full rise in about 8 seconds. Sections of the foam showed a density of about 0.6 pcf and were obviously much stronger than the 0.35 pcf material sprayed earlier.

The sprayed and cured foam was found to be only weakly sealed to smooth cardboard. Whole chunks of foam could easily be freed from the cardboard surfaces. A much improved adhesion was evident on the smooth concrete. In some regions it was apparent that adhesion to concrete was stronger than the cohesive force within the foam itself. Subsequent liquid penetration tests showed no significant penetration by dyed water.

Overall, the 0.6 pcf density material showed a definite improvement over the 0.3 pcf formulation, especially in the adhesion on concrete. However, when compared to a conventional 2 pcf material, the 0.6 pcf formulation was understandably inferior, both with respect to adhesion and strength. The results of these initial spray tests indicated that the 0.6 pcf formulation possessed the capability of substituting for the 2 pcf but in terms of strength alone was obviously less sufficient.

Additional Development and Evaluation

Unquestionably, the major weakness of the water-isocyanate foam was its apparent lack of adhesiveness. This was especially true because of its extreme lightweight and inherently weaker structure. Additional laboratory studies to improve adhesion consisted of adding water soluble polymers, especially film forming varieties, to the original water-isocyanate mix. The polymers were added to the water phase of the mix with the intent that the reaction with isocyanate would remove all water, leaving a dried film of polymer to improve adhesion and possibly cohesion. The results in general were unsatisfactory, however. Materials tested and the results are given in Table 10.

A series of spray tests were conducted on concrete in which the foam was applied 10 inches high in a 3 foot wide circle to form a container. Water was added to the inner area. With a four inch height of water, seepage at the concrete-foam interface was apparent. In addition, water was found leaking through channels which had inadvertently formed in the barrier wall. With about 5-6 inches of water, the barrier uplifted from the concrete. There was no evidence of fracturing or tearing of the foamed mass indicating that structurally the foam would serve well as a barrier if the problems of fixing it firmly to the substrate were solved. These results clearly indicated that because of the buoyancy the lightweight material probably required exceptionally good adhesion qualities, even to dry surfaces. Although the higher the expansion the greater the amount of material delivered from a portable unit, the unsolved problems would appear to limit the practical urethane systems to densities of 0.6 pcf or greater.

TABLE 10- TESTING OF SUPPORT MATERIAL TO IMPROVE ADHESION

Added Polymer	Concentration*	Results
Rhoplex B60A	50%	Good foam, poor adhesion
Polyethyleneamine	50%	Good foam, 0.5 pcf
Geon 351 (Latex)	50%	Poor foam
Hycak 1570	50%	Did not foam
PVA 570 (PVA 72-60)	5%	Good foam, poor adhesion
Sodium silicate	6%	Good foam, poor adhesion
PVA 205K	10%	Good foam, poor adhesion
Amisol	10%	Good foam, improved adhesion
Acrysol ES	10%	Poor foam
Primatloc	10%	Poor foam

*denotes the amount of solid polymer or additive in the water portion of the mix.

SECTION VII

HIGH EXPANSION FOAM COVERS

Spilled material contained either by artificial or natural barriers can still pose a major threat. Release of dangerous vapor can cause a toxicity hazard not only in the proximate location but in downwind areas as well. A potential fire and explosive threat may exist perhaps accentuated by the movement of men, equipment and existing circumstances. The danger to the clean-up crew may slow down that operation allowing time for ground water movement or other means of moving the contaminant into the water system. This phase of the report deals with the evolution of soft surfactant type foams which when applied to a spilled contaminant would form a protective covering.

Foam Resistance to Wind

Prevailing wind speeds are a major consideration in the application of detergent foam in open areas. Since foam covers will perform partially as a function of their thickness, it is necessary to have information on the effect of wind speeds. Preliminary tests were, therefore, conducted to determine the resistance of foam heights to various wind speeds. Tests were conducted in a wind tunnel in which foam was applied onto a liquid substrate. Trichloroethylene was contained in a tray measuring 1.5 feet wide by 2.0 feet long by 1.5 inches high. Various heights of high expansion foam were applied by conventional means onto the surface of this simulated contaminant.

The foam formulation consisted of polyethyleneimine, polyvinyl alcohol and MSA long lasting foam agent. This particular formulation was selected since it reasonably approached the type of ingredients which were expected ultimately to be used as a vapor barrier. The expansion of the foam used in these tests was about 200:1.

The test results were not able to establish clear-cut boundary conditions. Sufficient experience was gained to indicate that at 9 mph windspeeds all high expansion foam masses >4 inches could easily be uplifted and completely displaced from a liquid surface. The maximum allowable height in a 5 mph wind was about 4-6 inches. Even in this latter case it was strongly suspected that the ability of the foam to anchor onto the sides of the tray and the outside surfaces contributed some stability to the total foam mass. A foam height of 6-8 inches under the same 5 mph windspeed was obviously displaced from the liquid surface.

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These tests indicated vulnerability of high expansion foams to wind in the 5-10 mph range. Thus, maximum vapor suppression and protection should be accomplished with foam heights no greater than 3-4 inches.

Foam Candidates

In general, foamed masses are delicate systems whose properties are continuously changing with time. The stability of a foam is dependent upon a number of factors but the greatest threat to the life of the foam is posed by the chemical and physical properties of the contaminant. The numerous types of potential contaminants, each with its own unique properties, render it impossible to predict specific foam qualities suitable for all possible contaminants.

A screening program was designed in which various preparations and methods could be evaluated at least on a comparison basis. These screening studies were conducted in the system shown in Figure 13. A stainless steel holding tray (3-7/8 in. wide by 6-5/8 in. long by 3/4 in. high) was housed in a plexiglass box measuring 6-1/2 in. wide by 18 in. long by 9 in.high. A sweep of 50% RH air entered at one end of the box and purged the escaping vapors to the mixing chamber at the exit end. Volume flow of sweep gas was 0.6 cfm. All tests were conducted at ambient conditions ($\sim$70°F).

A typical test consisted of charging 120 cc of liquid contaminant to the holding tray. The exposed liquid surface area was 25.6 square inches. With the charged tray in place, the air sweep was activated. The free evaporation of the contaminant liquid normally resulted in depressing the temperature of the bulk liquid. In most cases, subsequent thermal equilibrium was established at a temperature several degrees less than room temperature. Samples taken at this time were indicative of vapor evolution from an uncovered source. At this point the test foam was applied by filling the entire box to the required height. The amount of contaminant vapor present in the gas phase was taken as a measure of the effectiveness of the foam cover.

The total volume flow of sweep gas was maintained constant for all runs. The significance of this is that as the applied foam collapsed the void space increased thereby decreasing the velocity of the sweep across the foam surface. It was felt impractical to maintain a constant velocity of the sweep gas especially where foams were collapsing rapidly. The variation in sweep velocity was of significance only in instances where deep beds of foams were examined.

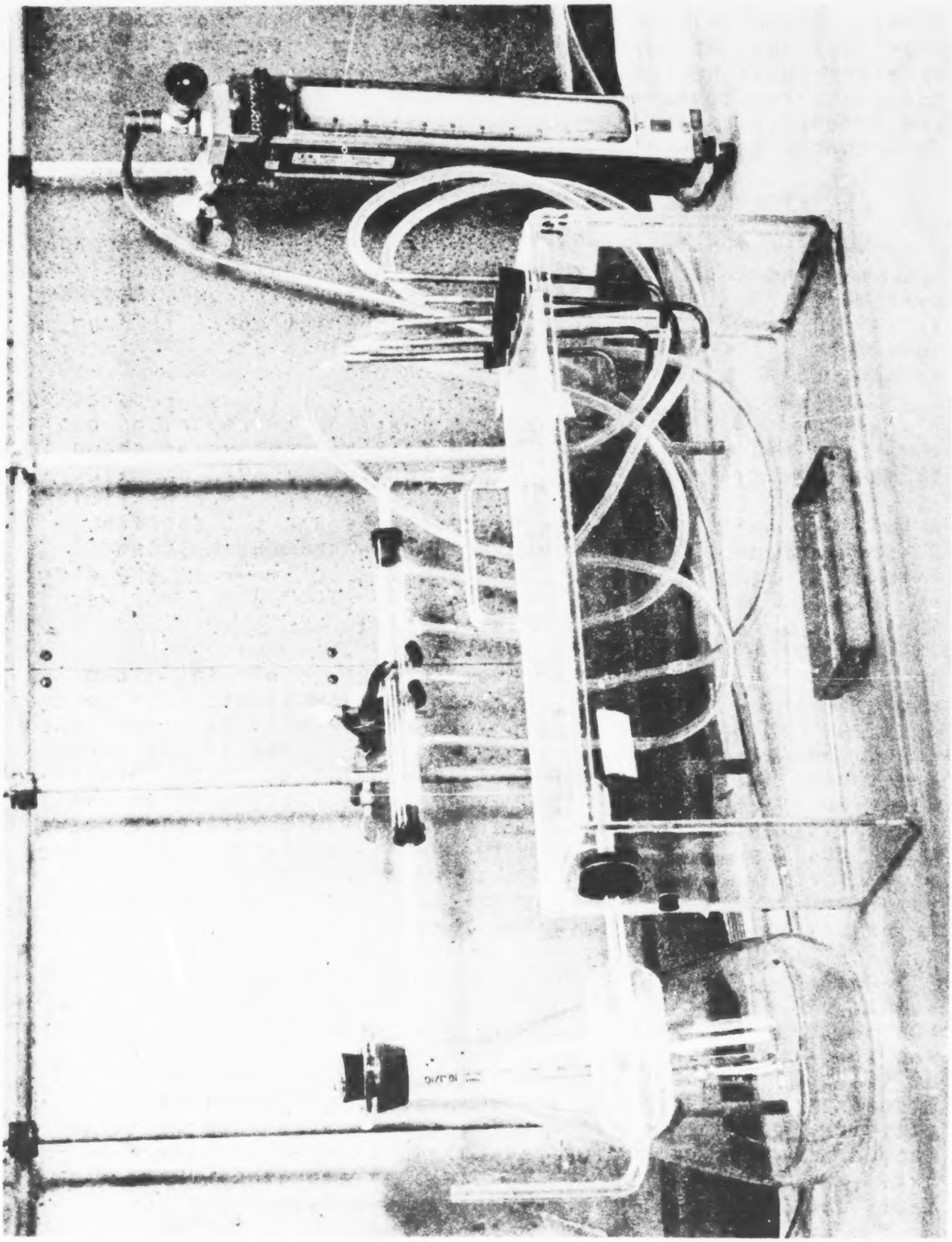
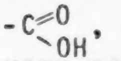


FIGURE 13 - LABORATORY SET UP FOR SCREENING OF HIGH EXPANSION FOAM CANDIDATE COMPOSITIONS

Initially, vapor analyses were performed using MSA detector tubes. These devices are selective, rapid and reasonably quantitative. As work progressed and the inadequacy of the detector tubes became apparent, analyses were performed using the gas chromatograph. This instrument is extremely selective and offered a capability of coping with a several thousand fold change in concentration.

Conventional Foams

A conventional fire-fighting foam was evaluated to determine the covering capability of material which would be readily available. MSA standard fire fighting foam was selected as a typical material and toluene as the contaminant. The selection of toluene was based on its relative chemical inertness or absence of reactive functionalities (-OH, $>$C = 0,  $-C\begin{matrix}\nearrow 0\\ \searrow OH\end{matrix}$, etc). Toluene is lighter than water and is also a very poor solvent for water;hence it would not be affected by the foam drainage.

A 6.5 inch height of foam was applied to the toluene from a 3% solution of MSA foam agent using the generator shown in Figure 14.

The collapse of the foam was evident almost immediately. After about 15 minutes of contact with the liquid toluene, the initial 6.5 inches of foam cover had completely collapsed exposing the liquid surface. The normal collapse rate for this foam in the absence of environmental effects is 8-10 inches per hour. A single sample taken 12 minutes into the run showed a toluene content of 125 ppm in the sweep gas phase versus a value of >800 ppm for the uncovered toluene. Actually, the 800 ppm level is the maximum quantity of toluene which could be reliably detected by the detector tubes. Subsequent analyses by the gas chromatograph showed toluene vapor evolved from an uncovered tray in this type of test to be several times this value.

An additional test was performed using a 6% solution of foam agent. The results were similar -- complete collapse of the foam within 20 minutes. The rate at which this foam collapsed was surprising especially in view of the presumed inertness of the selected contaminant. These data must not be construed as demonstrating the complete ineffectiveness of existing foam agents. Actually, the limited data collected showed a very significant reduction in vapor evolution up until the foam collapsed. In cases of emergency where other facilities and materials may not be available, the use of

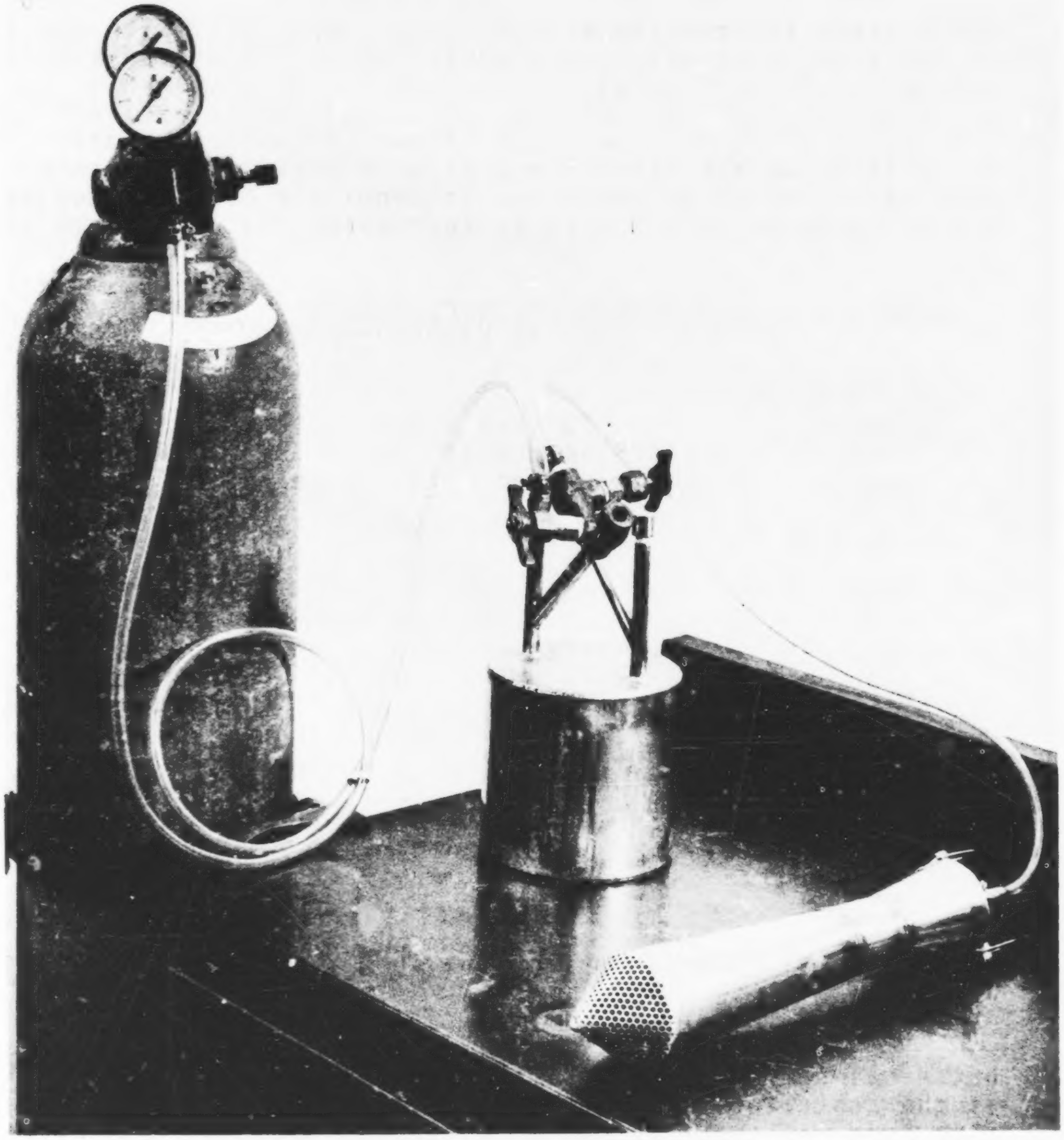


FIGURE 14 - LABORATORY FOAM GENERATOR SYSTEM

existing foam agents could provide a useful service. These laboratory data indicate that the beneficial effects would be short lived but repeated applications could be made.

Long Lasting Foams

Since vapor suppression was obviously associated with the life of the foam, a proprietary preparation of MSA was of special interest. This formulation consists of polyethyleneimine, polyvinyl alcohol and MSA foam agent and in the past had been the source of foams with lives of over 3 months or more. Table 11 shows the performance of an 8 inch layer of this foam generated at an expansion of about 200:1. The results can be compared to a 0.5 inch layer using the same formulation but dispensed at an expansion of about 4:1. Toluene served as the contaminant in both cases. In the latter case, the fine foam was generated using blow pipes equipped with fine fritted ends. The results obtained in both cases showed a marked improvement. Of equal importance was the significant vapor suppression achieved by exceptionally thin beds of the

TABLE 11 - COMPARISON OF THICK VERSUS THIN LAYERS
OF FOAM COVER ON LIQUID TOLUENE

Elapsed Time (min)	Toluene Vapor Content (ppm)* 0.5 in. Cover Low Expansion (4:1)	8 in. Cover High Expansion (200:1)
Uncovered	>800	>800
30	34	20
45	12	
60		45
110	12	
140		55
175	50	
230	50	Foam collapsing
240		100
260		300, liquid surface exposed
16 hrs	250	

*Toluene vapor content in air sweep

foam. The data shows excellent vapor suppression up to 16 hours which was the effective life of this covering. Ordinarily, the collapse of this foam during a similar time period but without the presence of a contaminant would have been less than 0.1 inch.

New Foam Development

The results of these preliminary tests showed:

1. the limitations of existing fire fighting foam agents
2. the effectiveness of thin but densely packed beds of foam
3. the adverse effects on foam life posed by the contaminant.

Emphasis at this time shifted to a foam cover which could cope with the more chemically reactive species such as alcohols, ketones, etc. These materials are not only produced in large quantities but were known to be effective poisons for surfactant foams.

The most difficult class of compounds to smother effectively are the low molecular weight, volatile, highly polar solvents with methanol as an outstanding example. Most foam preparations collapse instantly on contact with the alcohol. With continued addition of foam solution the subsequent foam drainage alters the alcohol surface tending to decrease the adverse effects giving a false sense of foam stability. On a practical basis, however, where large spills were involved, such dilution would not occur.

For the purpose of further materials screening, methyl alcohol was selected as the test contaminant. Three approaches were taken which showed considerable promise. These included: solution of silicates which formed a relatively hard layer of solid silicates on the surface of dry methanol, solutions of pectin, which formed a gel on the surface and solutions of Acrysols which also formed a thick rubber-like coating on top of the methanol. Both these latter types of cover eventually dried to a hard impervious crust. All three materials were best applied from a low expansion system.

Silicate System

The silicate solution employed was a commercial grade water solution containing approximately 30% of dissolved sodium silicate. This solution was diluted with approximately an equal portion of water and a foaming agent added to maintain its concentration at about 4%. Foams blown from this formulation collapsed on contact with dry methanol; however, a dense, crystalline structure resulted. If applied at a high expansion ratio, insufficient material was available to form a continuous blanket. In that case the crystallized segments sank. At low expansion, the generated foam "froze" into a solid mass with sufficient entrapped air to remain buoyant. Subsequent tests showed that the silicate formulation was effective for methanol but was not suitable for other non-alcohol type materials, polar or otherwise.

Acrysols

The Acrysols are a class of acid type polymers which when neutralized by a base form a solid gel. A foam of this variety is difficult to prepare since gellation occurs immediately upon contact with the base. Low density foams could be produced by using solutions of sodium bicarbonate. The CO_2 liberated from the mix served as a blowing agent to expand the foam.

In contact with alcohol the gelled foam formed a thick coating which tended to float on the surface of the alcohol. Some dissolution of the gel occurred but the rate was slow. This type of polymer was also an effective cover for ammonium and amine type compounds where gellation occurred upon contact. Like the silicate, it was limited to a small group of materials.

Pectin Type Foams

The most widely applicable foam was prepared from citrus pectin. Pure citrus pectin is a powder which dissolves readily in water provided sufficient mixing is available. It is commercially available in preparations offering a range of set times and thickening power. Chemically, citrus pectin is a weak acid and maximum thickening is achieved at a pH of about 3.1. Once the added powder is adequately dispersed, wetted-out and dissolved, the process of thickening begins. Normally, a 1.5 to 2.0% solution of pectin in water becomes viscous within 30-60 seconds. On a practical basis some thickening of the solution begins immediately following the introduction of the powder. Foams generated immediately after dissolving the pectin showed exceptional capabilities of minimizing the evaporation of a number of substances. Similar to the above systems, maximum results were obtained by applying the pectin in a low expansion (30:1) form. It was successful in part because the contaminant was swamped with the pectin solution. Immediately upon contact, the foam collapsed slightly but entrapped finely divided air bubbles, forming a tough impermeable buoyant skin on the surface of polar contaminants. With the non-polar type, contaminant skin did not form but the foam remained intact behaving somewhat similar to conventional type foam agents. In both cases, however, the foam eventually thickened and dried to a permanent structure.

The data obtained with pectin solutions is presented in Figure 15. The data is shown as the percent reduction of vapor found in the gas phase with the uncovered samples used at 100%. Effective reduction in vapor evolution was achieved for a variety of compounds with different chemical entities. The results achieved with these formulations and especially with solutions of pectin were exceptionally promising. They were able to be floated on a variety of materials,even methanol and acetone with quite low liquid densities, with good control of vapor release.

These results were obtained by mixing 4 gms of citrus pectin (Eastman Chemicals, Cat. No. P2569) in 200 cc of water and adding 4 gms of a foaming agent such as MSA salt water foam agent. The pectin powder was added to the liquid solution of water and foam agent in a blender and mixed at high speed for 10 seconds. Foam was blown using a blow tube with a fine fritted end to produce small bubbles. Foam produced in this manner was generally expanded 2-5 fold. It was difficult to control the expansion ratio since the properties of the solution were changing rapidly. Normally, the height of the cover rarely exceeded 0.5 inches above the liquid surface. Analyses in these tests were performed using a gas chromatograph. Samples of the contaminated sweep gas were taken in a 1 cc hypodermic needle and injected directly into the gas chromatograph.

There are some inherent disadvantages to the use of pectin. Water is the only solvent and because of the viscosity problem, the maximum concentration of pectin in water is limited to about 1%. Further, once the pectin is added to the water the properties of the resulting solution begin to change. Thus, the characteristics of the solution exiting at a foam nozzle depend upon the pectin dwell time in the line. Fortunately, dwell time can be controlled by inserting the pectin into the water line near the nozzle, at the pumper or at intermediate locations.

Introduction of the pectin into standard systems posed some problems, however. A powder eductor was examined as the first means of introducing pectin into a hose line. This

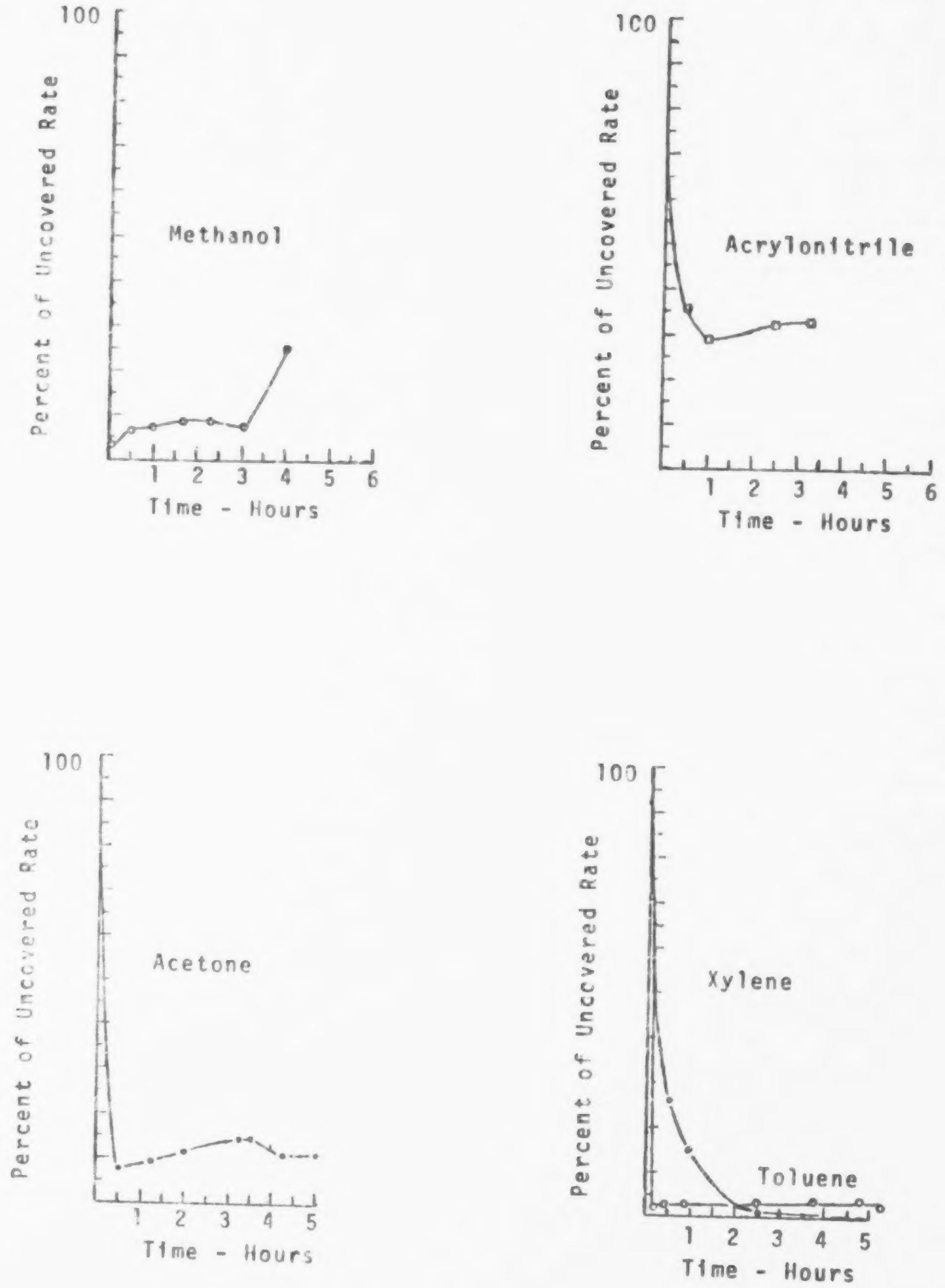


FIGURE 15 - VAPOR SUPPRESSION OF TYPICAL HAZARDOUS MATERIALS BY PECTIN MODIFIED FOAM COVER

device consists of a large funnel attached to the intake of an eductor. Sufficient pectin could readily be injected into a 10 gpm water line to maintain a pectin concentration of well over 2%. The exiting water solution was collected and showed the pectin to be finely dispersed with no obvious lumps or aggregates of undissolved powder. To add both foam concentrate and pectin into the line at the same time, two approaches were examined: (1) a completely powdered system containing a solid surfactant blended into the pectin and (2) a stabilized suspension of pectin in a liquid surfactant. The latter system would be more consistent with existing foam dispensing equipment.

Subsequent laboratory studies showed powdered amphoteric surfactants to be excellent foaming agents for pectin. A powdered mix was prepared by blending 1 part surfactant to one part pectin. The problem of preparing a free-flowing, stabilized suspension of pectin was only partially solved. The best formulation consisted of equal parts by weight pectin, a liquid alkylaryl surfactant and propyl alcohol as a viscosity modifier. The resulting suspension was only temporary and complete settling of the pectin occurred within 24 hours.

Several attempts were made to spray the two pectin concentrates using conventional fire-fighting type generators. The solid blend of foam concentrate and pectin was evaluated in a Feecon type low expansion nozzle. Materials were pre-blended in a 1:1 weight ratio. Two tests were completed with the funnel eductor installed at two different locations along the hose line to provide a dwell time of approximately 5 and 50 seconds. Output foam of the low expansion nozzle was directed onto 2 feet wide by 4 feet long trays containing about a 2 inch depth of dry methanol. The output foam in both cases was exceptionally poor when compared to a conventional foam agent used alone. The pectin foam was dispensed as a heavy, wet foam which caused excessive splashing and dilution of the alcohol. Some foam cover did develop with the shorter dwell time. However, the solution runoff was exceptionally gritty indicating the pectin had not completely dissolved. In both cases, dilution of the alcohol had occurred to render the test results inconclusive. It was obvious that a major problem existed in duplicating the quality of the foam used in the laboratory tests.

An attempt was made to produce a high expansion foam starting with the liquid "suspension" or slurry of pectin and surfactant described earlier. The generator was of conventional design and capable of expansion of 200-300:1. The liquidized pectin was uplifted into the line via an eductor at a location yielding a dwell time of about 20 seconds. A reasonably high expansion foam was produced but was found to collapse readily on contact with the alcohol. Samples of the runoff and drainage again indicated that the added pectin was not completely dissolved.

Small scale tests were next performed in the laboratory using a miniature spray system. The device consisted of a 0.5 gpm spray nozzle and a flat screen of about 1.5 inch diameter. The entire spray head or generator was housed in a cylinder measuring 1.5 inch diameter by 3 inches long. The system operated batchwise; that is, a foam solution was prepared and charged to a pot. Pressurized nitrogen or air (100 lb psi) fed the solution to the generator. The study portion of the effort consisted of charging the pot reservoir with water, then when all was in readiness, quickly adding the pectin mixes followed by foaming. Various time delays were examined between adding the pectin and the actual foaming. Results showed that optimum foam cover was developed with a 30 second dwell time. Foams produced at this time were thick creamy mixtures which formed excellent covers on methanol and acetone. With holding times greater than 30 seconds, the expansion ratio decreased until at one minute the foam output was only slightly higher than 1 to 1. Even at the lowest expansion the foam (or aerated solution) formed an excellent cover. If dropped from any height, this material sank deeply into the alcohol but immediately surfaced and remained buoyant.

The results of these tests indicate that although quality foam can be produced, a requirement would exist to maintain control over the operating conditions. Undoubtedly, the source of the difficulty can be traced to the rate at which the pectin is dispersed, wetted out and finally dissolved. If the foaming process is carried out prematurely, insufficient pectin is dissolved to form an effective cover. On the other hand, unnecessary delays in foaming allow the solution to thicken in which case only high energy type generators would be effective.

Expanded Rigid Systems

Urethane

The success indicated by the skin or film formers led to an examination of other type materials which could be floated onto methanol, acetone, etc. The use of more rigid lightweight foams which could be generated in place and floated onto the spill was next examined. Since urethane was available it was of interest to adapt this form to the present need. Undoubtedly, urethane foam could be generated at the spill site and merely floated onto a contained spill. Thus, thin sections of urethane could be generated and "welded" by additional urethane mix to generally cover an easily accessible area. However, this approach similar to stretching a plastic sheet across the spill would be at a serious disadvantage in rough terrain or where tall weeds or grass were present and might hinder cleanup operations. To circumvent this difficulty, a limited effort was applied to the generation of urethane "snow". The intent was to spray tiny droplets of a quick rise urethane mix into the air and have the material expand fully by the time it fell onto the solvent. If such spheres were sufficiently small they could effectively flow into and around most obstructions.

Discrete but irregularly shaped balls of urethane were successfully generated by using an excess of gaseous Freon to propel the liquid mix from the nozzle gun. An additional line carrying the Freon gas was fed to the mixing nozzle to break up the liquid mix into fine droplets. The generated urethane was allowed to free fall onto trays of alcohol. Although some urethane was sufficiently blown and cured to float on the alcohol, most of the deposited urethane was still in the blowing stage with the result that it sank or dissolved into the alcohol. The output of foam was small and consumption of gas was extremely high and it was concluded that this approach was a relatively poor risk for further development.

An attempt was made to apply shredded urethane foam onto alcohol. Invariably, all attempts to shred the cured urethane resulted in the production of great deals of powder with no cell structure. This material in contact with alcohol was wetted out and rapidly sank.

Microballoons

An examination was made of the applicability of tiny hollow spheres both as a cover and as a support media to provide additional buoyancy. The properties of these phenolic type balls are given in Table 12. In the first test a layer of spheres up to 1/4 inch deep was applied over the methanol. Analyses showed no significant vapor suppression occurred during a one hour test. In the second test the spheres were added to the pectin foam after the powdered pectin was first dissolved in the blender. The weight ratio of pectin to spheres was 2:1. The spheres had a tendency to float on top of the applied foam rather than be incorporated into the foam matrix as intended, and the pectin-sphere combination was no more effective than pectin alone.

TABLE 12 - TYPICAL PROPERTIES OF PHENOLIC SPHERES
(BJO-0930, Union Carbide Plastics Co.)

Average particle size (dia.), inch	0.0017
Particle size range (dia.), inch	0.0002-0.005
Bulk density, pcf	3-5
True sphere density	12

SECTION VIII

SYSTEMS SUMMARY

The purpose of the program was the evolution of systems which could be used in the control of hazardous chemical spills from a transporting vehicle. Although the development effort cannot be considered complete, significant progress was made with the polyurethane and foamed concrete systems. Both systems can be considered for control in a number of potential situations. The following paragraphs will synopsize the status of both materials, the equipment, their characteristics and the current limitations.

Polyurethane

The basic objective of the polyurethane development was the adaptation of existing commercial equipment to the spill control application. Two portable units have been evolved. The small unit is hand portable, the larger is available as a back pack or cart mounted unit. Pertinent details are given in Table 13.

TABLE 13 - POLYURETHANE SYSTEMS

	Model I	Model II
Part No.	510028	210029
Vol. of foam delivered	22-25 cu ft	50-55 cu ft
Delivery rate (avg.)	5 cfm	5-7 cfm
Weight (gross)	27 lbs	65 lbs
Size (in.)	20x10x5	20x20x10
Storage time (tentative)	6 mos.	6 mos.
Storage temp.	above 50°F	above 50°F
Useful temp. range (substrate)	15° to 120°F	15° to 120°F

Operating instructions are provided on the package. The polyurethane is dispensed from each unit in a spray cone as a thick liquid. There is a delay time of some 8 to 12 seconds after generation before foaming begins. The foam rigidizes rapidly after expansion. The rigidized foam is inert to a wide variety of chemicals and when bonded to the substrate can effectively contain or divert chemical spills.

The polyurethane formulation bonds well to dry surfaces such as cement, asphalt and packed dirt. The material also bonds to itself,thus new foam can be effectively deposited over old foam. Control on dirt may be limited with failure occurring due to liquid seepage through the substrate at the dirt-urethane interface.

Some control is exercised on gravel, rocky or vegetated ground. Some penetration will ultimately occur below the substrate-urethane interface. In such situations double or triple barriers can be set to extend the time of control.

Temperature also has an effect. The unit temperature at the time of use should preferably be above 50°F, but at least above 40°F. Substrate temperatures can be as low as 15°F. At the lower temperatures expansion may be reduced at least for that material applied directly to the substrate.

At the present time good adhesion is not obtained on wet surfaces nor can flowing streams be directly blocked. If the foam can be mechanically locked onto the surface the problem of wet surfaces can be overcome. This is the case with sealing storm sewer grates, manhole covers, etc. By generating foam into a plastic or rubber bag, pipe, culverts and the like can be plugged even when liquid is flowing.

Although the chemical nature of polyurethane would indicate resistance to most chemicals, actual evaluation is limited. Control has been demonstrated for water base liquids except strong acids, non-polar organics, and some selected materials as chlorine and ammonia. Polar compounds are a question. It has been established that the present formulation is not effective against methyl alcohol.

Foamed Concrete

The objective of the foamed concrete task of the program was to demonstrate the feasibility of erecting a fast-set foamed concrete dike and to outline the general requirements for an emergency field unit. Both objectives have been achieved.

Foamed concrete of density about 40 pcf can be made to take an extremely fast set (2-3 seconds) with the addition of sodium silicate to form a gelled structure with sufficient strength to build dikes 2 feet high or better. The equipment requirements are simple. A unit following the schematic of Figure 16 would consist of a mixer for blending a cement-water slurry, a slurry pump, preformed foam generator, sodium silicate solution, storage tank and nozzle. The preformed foam is metered into the slurry stream where it blends to produce foamed concrete. The silicate solution is injected as the foamed concrete exits the nozzle, producing a chemical reaction with the cement to cause the rapid set.

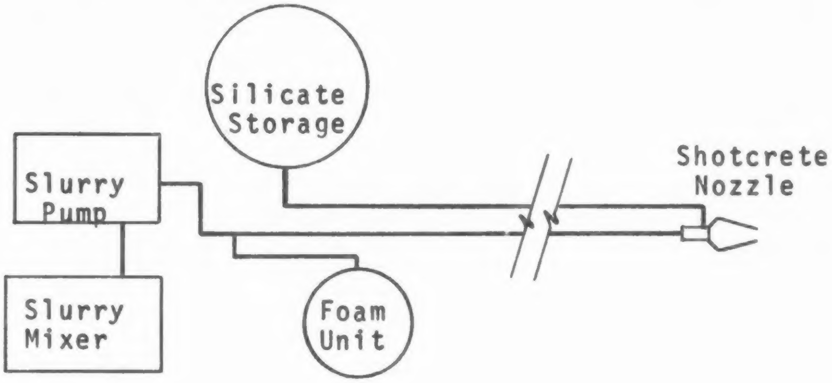


FIGURE 16 - SCHEMATIC OF FOAMED CONCRETE SYSTEM

A foamed concrete barrier has strength enough to impound liquid immediately after being placed, and flowing water of slow stream velocities has been successfully pooled. The initial gel set has surprising strength, but to impound liquids to any appreciable depth, such as two feet, behind the barrier needs additional strength from the hydraulic set of the cement. This comes on slowly after the initial gel set and is a function of many factors including water temperature, water/cement ratio and type of cement. Under ideal conditions significant strength from the hydraulic set could be attained in less than 5 minutes. Thus, the rate of build up of hydraulic head on a newly poured barrier is probably the single most important factor to successfully impounding a spill. For this reason, broad, flat rather than narrow, high-pitched impounding basins are favored.

The type of substrate is not an important factor. Tests on clay, shale, chipped limestone, grass and weed-covered ground have been successful. In addition, such chemicals as methanol, 1,1,1 trichloroethane, phenol, acetone cyanhydrin and acrylonitrile do not appear to affect the gel set action.

As might be expected in a water-based system, extremely cold, sub-freezing working conditions make the equipment operations difficult. The preformed foam and solution lines tend to freeze first. The use of freezing point lowering additives in the solution has only had moderate success.

A suggested design for an Emergency Field Unit was shown in Figure 12. The unit consists of the basic components described earlier, driven with hydraulic motors. A gasoline engine furnishes power to the hydraulic pump and a small air compressor. The components are all commercial off-the-shelf items. The parts list is given in Table 14.

The unit is trailer mounted, suitable for a pick-up truck operation. It will produce approximately 50 ft^3 of foamed concrete at 45 pcf per batch within 30 minutes of delivery to the site. Repeat cycles would take approximately 25 minutes each.

Three such batches (150 ft^3) could be produced in approximately 80 minutes to build barriers of such sample dimensions as:

2 ft x 2 ft x 38 ft
1.5 ft x 2 ft x 50 ft
1.5 ft x 3 ft x 33 ft

TABLE 14 - MOBILE FOAMED CONCRETE EMERGENCY UNIT

Item	Quantity	Description
1	1	Ingersoll-Rand Air Compressor, Type 30, Model 71T2XGT with gas engine drive, Wisconsin Model V465D engine and V-465D power take-off clutch. Gasoline tank included with motor.
2	1	Hopper similar to MSA P/N A91959, 400#
3	1	Agitator blade similar to MSA P/N 379689 Agitator B91962
4	2	Bearings, P/N 66802
5	1	Slurry pump, Moyno 3L4, P/N 68572
6	4	Motor, hydraulic, Char-Lynn Size AA
7	1	Pump, hydraulic, commercial shearing P30 Series, 1 1/2 in. gear
8	1	Silicate proportioning pump, Viking Model HL124S, carbon bushing and stuffing box, all iron, built in relief
9	1	Foam pump, Viking Model HL156, all iron, built in relief
10	1	Foam tank, similar to pressure tank paint container
11	1	Foam gun
12	1	Hydraulic tank, P/N 456313
13	4	Couplings, T.B. Woods #6, P/N 625462
14	1	Speed reducer, Dodge No. 11
15	1	Valve, hydraulic - 4 way 3 position Double A P/N R6-175-FF-N
16	1	Valve, hydraulic - 3 way 2 position Double A P/N R6-175-FZ-N

Table 14 (Continued)

Item	Quantity	Description
17	1	Valve, hydraulic - flow control Double A P/N QXA175 with P15-06 sub plate
18	1	Filter, hydraulic P/N 625468
19	1	Strainer, suction P/N 69806
20	1	Breather and filler cap P/N 69081
21	1	Water control valve P/N 69412
22	1	Air on-off valve, 1 1/2 in. size P/N 69452
23	1	Gauge, hydraulic press, 0-3000 psi P/N 56414
24	1	Gauge, air pressure, 0-150 psi P/N 68052
25	1	Gauge, water pressure, 0-100 psi
26	1	Battery, Electric, 12V
27	2	Mounts for hydraulic motor with Viking Pump
28	1	Mount for hydraulic motor with Moyno pump
29	1	Mount for hydraulic motor with Dodge speed reducer
30		Hydraulic hoses
31		Hydraulic fittings
32		Compressor piping
33		Moyno pump piping
34	1	Sheave, hydraulic pump P/N 625869
35	2	V-belt P/N 69753
36	1	Mount for hydraulic pump
37	1	Trailer, Model 12001-2 double axle 12,000 lb capacity

Table 14 (continued)

Item	Quantity	Description
38	2	Bearings, pillow block, 1 15/16 in. dia P/N 66058
39	1	Stub shaft for mounting drive sheave
40	1	Coupling, T.B. Woods #7, P/N 63951

Raw materials for one batch are:

10 bags of cement (940 lbs)
30 gallons of sodium-silicate solution
1.5 quarts of foam concentrate

Material for one run would be transported on the unit. Material for three batches would weigh approximately 4900 lbs and require about 1300 lbs of water (215 gal.) at the site. Additional material could be brought in if needed.

The sodium silicate and foam concentrate would be the only material required to be stored in quantity for multiple batches. Enough Type I cement could be stored for 1 to 3 batches, with additional cement picked up as needed.

A detailed description of the procedure for placing the mobile unit in operation, with estimated time commitments for 2 men, is as follows:

Operation	Time (min)
Start gasoline engine, slurry and slurry mixer	2
Attach water source, fill tank to level mark (70 gal.)	8
Add cement (10 bags)	5
Add 1.5 quarts of MSA Reg Foam concentrate to 10 gal. foam tank -- fill with water to level	4
Attach silicate drums to pumper	2
Attach foam cement and silicate quick connect hose to unit	2
Total	23 min

The first cycle including set up and a run time of 10 minutes should require approximately 33 minutes. Additional cycles should be possible in less than 25 minutes.

Foam Covers

The evolution of a foam system capable of providing an effective cover for all chemicals was not fully completed during the course of the program. One prime class of materials, polar organic compounds,proved difficult. A pectin fortified foam was evolved which was effective for this class of materials but a generating system suitable for field use was not delineated. As a consequence, no large scale foam evaluations were conducted.

The tests which were conducted, coupled with prior work, do provide some useful data on foam covers. Although it is preferable to utilize a foam designed for use as a foam cover, in emergency situations the type of foam generated from fire fighting foam generators and agents may provide some benefit. Such foam should be used with caution. It should be applied to the greatest depth possible preferably greater than 12 inches deep and topped off or recovered with new foam when the depth collapses to 12 inches. It can provide some degree of control on neutral or alkaline aqueous solutions and nonpolar organic compounds of low volatility. The polar compounds as well as acids will destroy it. High volatile liquids will be afforded only partial protection since vapor release will cause holes or chimneys in the cover. With liquids with boiling points below 0°C a frozen layer will tend to form between the foam and the chemical which will slowly minimize the chimney effect.

Not all foam agents will provide suitable foam covers. In some cases a combination of foam and chemical characteristics will actually exaggerate the spill hazard. Commercially available fire fighting foam agents provide a broad range of collapse rates from 8 to 90 inches per hour as well as wide latitude in water drainage. Some drain as much as 70% of their water in 2 minutes. The better agents give up less than 50% of their water in 30 minutes.

The consequences of fast collapse are obvious. Those of fast drainage are not as clear but more serious. The loss of water causes two problems -- it reduces the weight and integrity of the foam and drains water into the underlying chemical. Dry foam is more subject to wind shear effects. Thus wind can cause disruption of the foam cover. In some cases foam masses can absorb quantities of the underlying chemical. If these are toxic or explosive, foam masses torn loose and blown away by the wind can be hazardous of themselves. Foam masses containing explosive vapors can be detonated.

It should be realized that foam blankets serve two purposes -- they isolate the surface from external effects which is important for flammable or explosive liquids, and reduce the vaporization rate of the chemical where such vapors are toxic or explosive. They do not control vaporization by providing an overpressure but by insulating the liquid surface from radiant energy. Water draining into the contained spill has an adverse effect on this insulating action. If the spilled chemical and water are miscible, the heat of solution can actually adversely effect the spill situation. This is truly a problem in the case of materials such as anhydrous ammonia where the heat of solution is very large.

By using a long lasting foam such as the polyethyleneimine system of MSAR (Type L Foam), collapse and drainage are controlled to low rates. Drainage is of the order of 40% in 30 minutes with collapse rates of 0.1 inches per hour or less. The foam has greater integrity, is less susceptible to wind effects and is useful with acidic liquids. These foam agents can be used in standard high expansion foam generators. Air aspirating units such as the MSA Mini-X which deliver 250:1 to 350:1 foam are preferred since they provide a heavier foam density and can be operated from a fire pumper. These hand-held units can deliver up to 7000 cfm of foam.

It should be cautioned that the use of a foam cover should in no way change the procedures which would be employed to handle the chemical without it. Its purpose is as an extra precaution. Further, whenever a foam cover is being applied, either initially or as a recover, those people applying the foam should wear full protective gear. Body protection such as the Acid King clothing of Wheeler Protective Clothing Company with bottled oxygen or the butyl suit of MSA with a self-contained Chemox rebreather is recommended.

SECTION IX

REFERENCES

1. MSA Research Corporation, "Sampling for Red Rock", Rome Air Force Base, Contract No. AF30(635)-12289.

2. MSA Research Corporation, "Safety in Transport and Handling of Chemical Warfare Munitions, Eglin Air Force Base, Contract No. AF08(635)-3674.

3. Modern Plastics Encyclopedia, Vol. 48, No. 10A, 1971-1972.

4. Hoff, G. C., "New Applications for Low Density Concretes", Miscellaneous Paper C-70-8, U. S. Army Engineer Waterways Experimental Station, Vicksburg, Mississippi, May 1970.

5. United Kingdom Mines Rescue Service, Nottinghamshire, Darbyshire and Leicestershire District, "Use of Gypsum Powders in the Construction of Stoppings", National Coal Board, Hobart House, London (1969).

6. Halliburton Company, "New Mine Sealing Techniques for Water Pollution Abatement, FWPCA Contract No. 14-12-453, March 1970.

7. Huron Cement Company, Alpena, Michigan.

8. Dreyrup, A. S. (to E. I. duPont deNemours & Co.) U. S. Patent 3,492,250 (Jan. 27, 1970).

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